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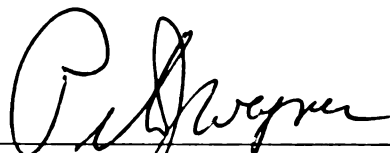
Photochemistry of Bi-functional Phenyl
Ketones Containing Remote Double Bonds

presented by

Keopyung Nahm

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry



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PHOTOCHEMISTRY OF BIFUNCTIONAL PHENYL KETONES
CONTAINING REMOTE DOUBLE BONDS

BY

KEEYUNG NAHM

A DISSERTATION

Submitted to
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ABSTRACT

PHOTOCHEMISTRY OF BIFUNCTIONAL PHENYL KETONES CONTAINING REMOTE DOUBLE BONDS

By
Keepyung Nahm

Alkenoxyphenyl Ketones

Intramolecular quenching processes of various alkenoxy-phenyl ketones were studied. The excited triplet benzene rings were quenched internally by the olefins when there were 3 or 4 connecting atoms between them; $-O(CH_2)_2-$ or $-O(CH_2)_3-$. The intramolecular quenching efficiency of the three connecting atoms system was better than those of the others by more than 100 times.

With $-O(CH_2)_2-$, the para- and ortho-alkenoxyphenyl ketones yielded photoproducts upon $>300\text{-nm}$ irradiation. From the para derivatives, the photoproducts were identified as substituted 1-acyl-8-oxatricyclo $[7.2.0.0^{5,9}]$ undec-2,10-dienes. From the ortho derivatives, the photoproducts were identified as substituted 1-acyl-6-oxa-tricyclo $[7.2.0.0^{3,8}]$ undec-7,10-dienes. The same types of products were isolated from the $-O(CH_2)_3-$ system.

The whole photoreaction is a two photon process; two intermediates were assigned for these unusual photoproducts.

In all cases the double bond undergoes ortho 2 + 2 cycloaddition to the benzene ring to give a bicyclo[4.2.0] octa-2,4-diene, which thermally interconverts quickly to a cycloocta-1,3,5-triene. This second intermediate is then converted to a bicyclo[4.2.0]octa-2,7-diene photochemically. This photostable bicyclooctadiene is converted at high temperature to the cyclooctatriene. The solvent effect on product formation showed that the excited states for this cycloaddition are triplet π, π^* states. From the internal quenching rate constants, the rate constants for interconversion between the two lowest triplets of the para-alkenoxyphenyl ketones were concluded to be $>10^8$ and $>10^{10} \text{ s}^{-1}$.

γ -Vinylphenyl ketones

The triplet lifetimes of various γ -vinylphenyl ketones were determined. The main product was acetophenone. The intramolecular charge transfer rate constants are $> 10^8 \text{ s}^{-1}$. They increased by 1.5-2.5 times with additional alkyl substituent on the double bonds. On the other hand, a δ -vinyl-valerophenone did not show efficient internal quenching. From these results, it was concluded that the quenching process requires a kind of 5-membered ring complex between the ketone chromophores and the olefin moieties.

TO MY PARENTS

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Most of all, I thank my wife, Jungok, for her love, support, and encouragement. I am also grateful to my parents and parents-in-law, and family for their continuous support.

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INTRODUCTION

In photochemistry, the excited states generated by an electron movement from the ground states to upper energy levels have large energy and they have to return to their ground states chemically or physically. Their lifetimes are short and their reactions are fast and internal energy of some photoproducts is too high to be made via ordinary thermal reactions. The main concern in photochemistry is usually the decay of an excited state to a ground state or a photoproduct.

In this part, general photophysics and photochemistry, the properties of excited states of phenyl alkyl ketones, and their related photoreactions will be introduced.

Photophysics and photochemistry - The photophysics of an excited state molecule can be described with a Jablonski diagram. Absorption of a photon promotes energetically a molecule from the ground state, S_0 , to an upper excited singlet state which rapidly undergoes internal conversion ($k_{ic} = 10^{11} - 10^{14} \text{ s}^{-1}$) to the lowest excited singlet.¹ The lowest singlet, S_1 , can decay to the ground state, emitting a photon of light (fluorescence) with a rate constant k_f of 10^6 to 10^9 s^{-1} or via radiationless decay with a rate constant k_d of 10^5 to 10^8 s^{-1} .¹ Photochemical reactions are possible from the excited singlet. The excited singlet can also undergo intersystem crossing to an excited triplet state ($k_{isc} = 10^7 - 10^{10} \text{ s}^{-1}$).

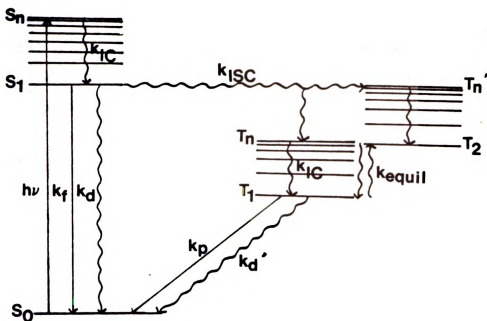


Figure 1. A Jablonski diagram for phenyl ketones.

This process includes spin inversion of an electron. Usually organic molecules have all paired electrons in the ground states. Therefore, this triplet state has two unpaired electrons.

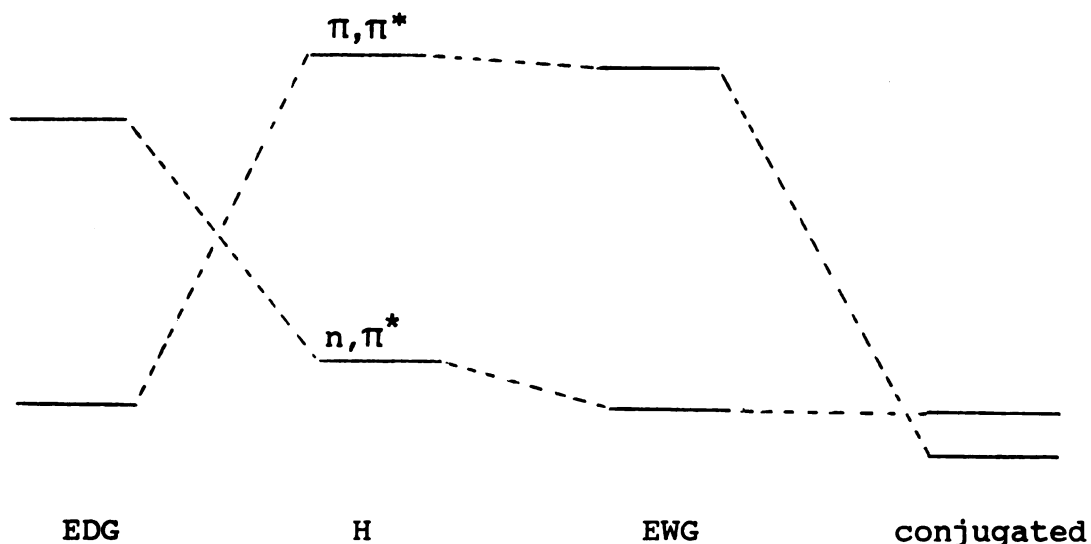
The excited triplet, just like the excited singlet, can undergo internal conversion with nearly the same rate constant as that of the singlet. Also radiative decay (phosphorescence) with a rate constant k_p of 10^{-1} to 10^4 s^{-1} , radiationless decay to the ground state, or chemical reactions are possible decay pathways from the triplet.

Ketone photochemistry - Ketone photochemistry is one of the most intensively studied areas in organic photochemistry

and has served as a good model for the understanding of fundamental questions. Even though the excited states of ketones have higher energy than most ground state species, the reactions from the excited states are now more predictable and explainable. However, photochemistry itself is one of the newest fields in organic chemistry and there still remain many questions unanswered.

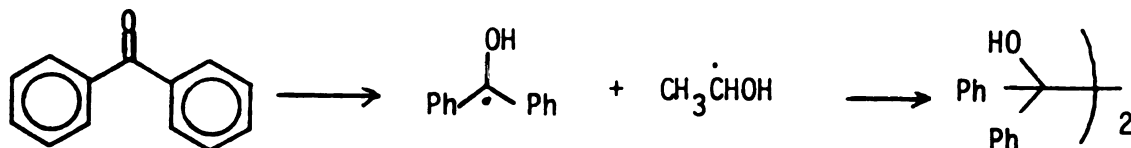
Phenyl ketones have n, π^* lowest singlets and their intersystem crossing rates are extremely fast ($k_{isc} = 10^{10} - 10^{11} \text{ s}^{-1}$) and efficient.² The quantum yield of the intersystem crossing in phenyl ketones is near unity.² In other words, every photon promotes a phenyl ketone from the ground state to the excited triplet.

Most phenyl ketones have two low lying triplets, an n, π^* and a π, π^* triplet, whose energy levels are affected by the ring substituents.³ In general, electron withdrawing substituents stabilize the n, π^* triplets relative to the π, π^* triplets and conjugating groups lower the π, π^* triplet energy levels.⁴



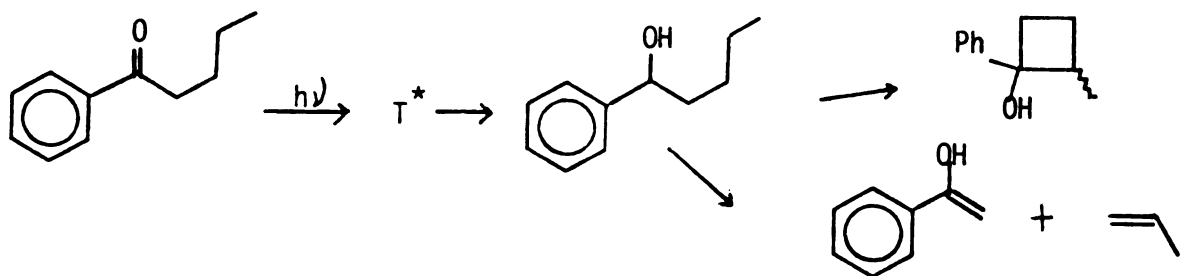
The n,π^* triplet comes from excitation of a nonbonding electron of the carbonyl to a π -antibonding orbital, thus has an electron deficient oxygen. The chemical behavior of the n,π^* triplet is similar to that of an alkoxy radical and hydrogen abstraction is the predominant reaction from the triplet.⁵ In a π,π^* triplet, excitation of a π electron to a π -antibonding orbital makes the oxygen atom slightly electron-rich and the hydrogen abstraction reaction slows down.⁵

Hydrogen abstraction of an n,π^* triplet ketone was first reported by Ciamician and Silber. When benzophenone was irradiated in ethanol, benzpinacol was observed as one of the products. It is formed by coupling of diphenylhydroxymethyl radicals, which are created by the hydrogen abstraction of the excited n,π^* triplet benzophenone:⁶



Intramolecular hydrogen abstraction was observed in 1934 by Norrish and Appleyard.⁷ When methyl butyl ketone was irradiated in the gas phase, the ketone photodecomposed to give acetone and propene. Ketones and aldehydes that possess γ C-H bonds undergo the photoelimination reaction, called the Norrish Type II process. This reaction involves 1,4-biradical via abstraction of a γ -hydrogen by the excited carbonyl oxygen.⁸ The biradical can either cleave into an olefin and the enol of a smaller ketone, or cyclize to a cyclobutanol which

provides a direct evidence for 1,4-biradical intermediate.⁸ This biradical was trapped by alkyl thiols⁹ and was detected by flash absorption spectroscopy.¹⁰ Theoretical calculations¹¹ also show that the 1,4-biradical can be formed as a product during the reaction of an excited ketone:



Substituted benzophenones (4-methyl or 4-trifluoromethyl) which have n, π^* lowest triplets are easily photoreduced by 2-propanol.¹² But, 4-phenylbenzophenone, which has a π, π^* lowest triplet, shows a 10^3 -fold decrease in reactivity compared to benzophenone.¹³ Similarly, the photoreduction of 4-trifluoromethylacetophenone (n, π^* lowest triplet) displays a six-fold increase in the rate of hydrogen abstraction, whereas 4-methylacetophenone (π, π^* lowest triplet) shows a ten-fold decrease in reactivity, both compared to acetophenone.¹⁴ Likewise, the Norrish Type II reaction of substituted butyrophenone and valerophenone follow a similar trend.^{3a, 15}

When the n, π^* and π, π^* triplets are close in energy, as in phenyl alkyl ketones, there is an equilibrium between these two triplets.¹⁶ The following Boltzmann distribution law describes the fractions of the upper and lower states with energy difference of ΔE at temperature T :

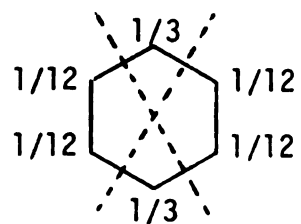
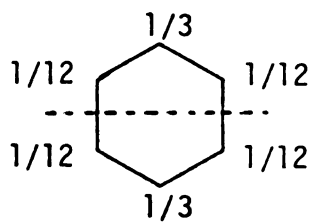
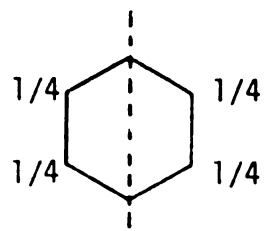
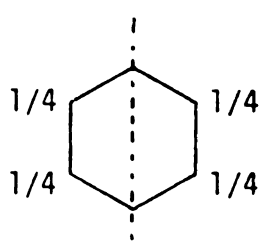
$$\frac{x_{up}}{x_{lo}} = \exp(-\Delta E/RT)$$

In case of p-methoxyphenyl ketones, the n,π^* triplets are located above the π,π^* triplets by about 3 kcal/mol, which means the n,π^* triplets have the equilibrium concentration of less than 1 % of the total triplets. These upper triplets still show the hydrogen abstraction, but the observed rate constant is only 1/100 that of the unsubstituted ketones.^{5,16} In this thesis, some unprecedented photochemical reactions from the π,π^* triplets will be introduced.

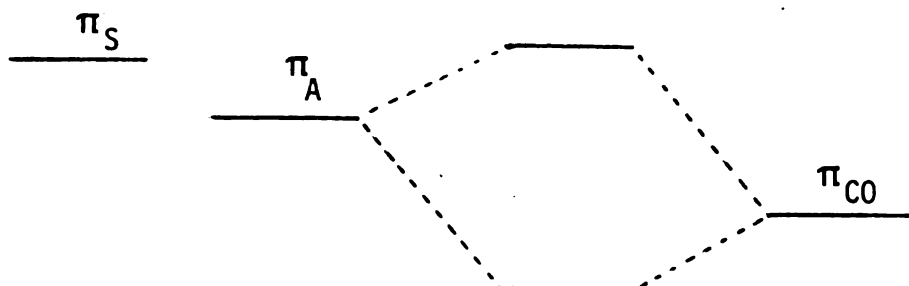
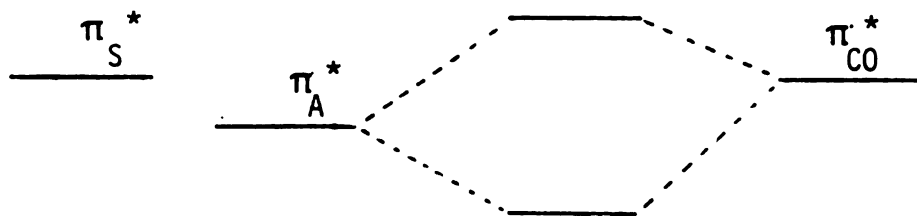
Although the spectral analyses of benzene and its derivatives have received considerable attention, the structure and the properties of these benzenoid systems in their excited states are not fully understood. However, much valuable information about the nature of π,π^* triplets can be obtained from the benzene study. Structural rearrangement on electronic excitation in benzene was first detected by de Groot and van der Waals when they noticed from the magnetic resonance spectrum that the lowest triplet state of benzene ($^3B_{1u}$) is distorted from the regular hexagonal structure,¹⁷ which is similar to that of S_2 benzene ($^1B_{1u}$).¹⁸

Theoretical¹⁹ and EPR^{19a,20} results indicates that the lowest triplet of benzonitrile (a model for acylbenzenes) is strongly 1,4-biradical in nature also. Conjugatively electron-withdrawing substituents (e.g., -CN, acyl) stabilize the anti-

Scheme I.

 π_A^*  π_A  π_S^*  π_S

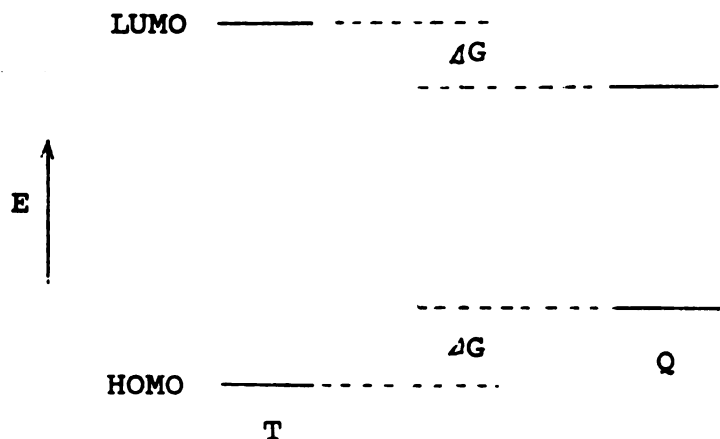
Scheme II



symmetric (in C_{2v}) π^* orbital and destabilize the corresponding π orbital such that $S \rightarrow L_a$ transition is predominantly $\pi_A \rightarrow \pi_A^*$ with little contribution from $\pi_S \rightarrow \pi_S^*$. The destabilization of π_A in ketones is caused by the mixing of π_A with the lower energy carbonyl π orbital.²¹ The π_A^* orbital is stabilized inductively as well as by strong mixing with the carbonyl π^* orbital (Scheme 1 and 2).

Quenching processes - Quenching of a triplet state can be performed by either energy or electron (charge) transfer. One of the requirements for energy transfer quenching is that the triplet energy of a quencher should be equal or less than that of a quenchee (for phenyl ketones, about 70 kcal/mol²²). Oxygen and conjugated dienes are good triplet quenchers in this case; the excitation energy of oxygen is 23 kcal/mol (singlet oxygen) and the triplet energies of the dienes are about 60 kcal/mol.²²

In case of electron transfer quenching, the positive hole created on the HOMO of a quenchee by electronic excitation



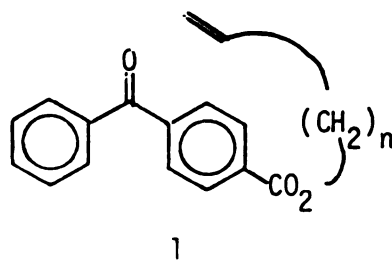
receives an extra electron (or charge) from the HOMO of a quencher, or the electron on the LUMO of a quenchee moves to the empty LUMO of a quencher, then each species returns to its ground state by the back electron transfer:²³

For the efficient electron (charge) transfer, either the oxidation potential of a quencher is smaller than that of a quenchee, or the reduction potential of a quencher has to be smaller than that of a quenchee. Weller derived an empirical equation for this process; the rates (k_{CT}) of fluorescence quenching of aromatic hydrocarbons are related to the differences in free energies (ΔG_{CT}) which are dependent on the oxidation potential of the donor ($E(D/D^+)$), the reduction potential of the aromatic acceptor ($E(A^-/A)$), the singlet excitation of the acceptor, and a Coulombic term.^{23a}

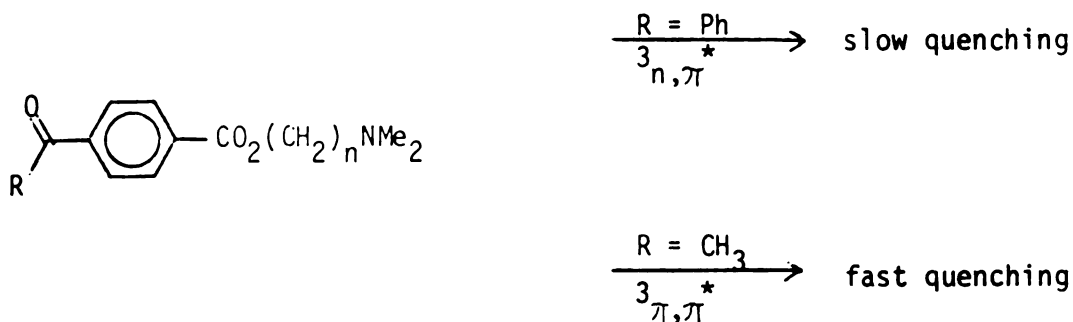
$$\log k_{CT} \approx \Delta G_{CT} = E(D/D^+) - E(A^-/A) - E(A_{0,0}) - e^2/\epsilon r$$

In the intramolecular charge transfer interaction, not only the thermodynamic properties of the donors and the acceptors but also the close orbital overlap between the donor orbital and the acceptor orbital (i.e. the accessibility of the donor) and the electronic configuration are important.²⁴

Winnik found intramolecular phosphorescence quenching of benzophenone chromophore in **1** occurs when $n > 8$ and decreases when $n > 13$.²⁵ These benzophenones have n, π^* triplets whose energies are localized mainly on the carbonyl group. The olefinic moieties can quench the emission intramolecularly only when they can approach the carbonyls to within 17 Å.



Wagner and Siebert²⁶ reported that regioselectivity of internal charge transfer quenching in some amino ketones depends dramatically on the electronic configuration of the lowest triplets:



For $R = \text{phenyl}$, the amino ketones have n,π^* triplets and show long-lived phosphorescence comparable to that of the model methyl ester derivative, $k \approx 10^5 \text{ s}^{-1}$. However, when $R = \text{alkyl}$, the lowest π,π^* triplets undergo very efficient intramolecular quenching, $k > 5 \times 10^8 \text{ s}^{-1}$. This study revealed that there is vast difference between n,π^* and π,π^* triplets in the position where the donor can feel sufficient overlap for electron transfer interaction and supports the concept of HOMO and LUMO orbital overlap in electron transfer reactions.²⁴

The study of photochemical intramolecular quenching in α -substituted ω -benzoylalkanes (n,π^* triplets) shows another example of significant overlap of the donor HOMO with the

acceptor LUMO. For the ketones substituted with SBu^{27} or NMe_2^{28} , the total number of atoms in these cyclic interaction equals $(n + 3)$ and the most rapid quenching appears when $n = 2$ or 3 which represents the formation of five- and six-membered rings. As n becomes larger, the k_{CT} decreases roughly by 10 times with each additional carbon chain, reflecting the expected decreased probability of forming medium-sized rings. When X is vinyl, overlap between two π orbitals also becomes an important factor in the quenching. β -Vinyl phenyl ketones undergo efficient intramolecular charge transfer quenching upon irradiation, which induced cis-trans isomerization²⁹ and also gave photoproducts.³⁰ Intrinsically this quenching is not rapid as expected from the comparison of the ionization potential of the olefins and the ketone, therefore the γ -vinyl

Table 1. Rate constants (10^7s^{-1}) for internal quenching in triplet $\text{PhCO}(\text{CH}_2)_n\text{X}^{29}$

n/X	SBu	NMe_2	$\text{CH}=\text{CH}_2$
1	130	<10	
2	460	430	80
3	240	740	<10
4	14	50	
5	<2	20	
intra	30	300	0.8

ketone ($n = 3$) still undergoes the type II reaction in relatively high efficiency.³¹ The quenching processes of these vinyl ketones were further studied in this thesis.

Photocycloaddition - There are many examples of photochemical reactions of bichromophoric systems. Among them, cycloaddition reactions of arenes to olefins are introduced here. The triplet version of these reactions was studied in this research. The reactions of bichromophoric systems can be divided into two groups; the intermolecular and intramolecular reactions. Intramolecular interaction could be faster than its intermolecular version if two chromophore can reach together. Also the reaction could be more stereospecific because of geometric limitation.

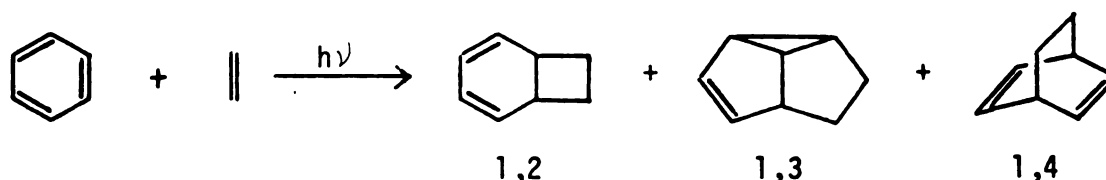
Since the discovery of fulvene from the irradiation of benzene,³² this unexpected lability of the benzene ring induced considerable research interest, and mechanistic and



theoretical problems in the area; i.e., photoisomerization of the benzene ring itself and bimolecular reactions.

Irradiation of mixtures of benzenoid compounds and olefinic systems gives rise to various products, obtained by adding the olefinic component across the 1,2-, 1,3- or 1,4-positions of the aromatic ring. From an orbital symmetry analysis of the systems,³³ it was deduced that 1,2-addition

was allowed from S_1 ethene plus S_0 arene, whereas the 1,3-addition required S_1 arene and S_0 ethene: in both cases, these dictates could be circumvented by mixing of states, and either could result from charge transfer excitation or if exciplexes were involved as adduct precursors.³⁴ Empirically it is known that 1,3-addition is preferred³⁵ to 1,2-addition, when the ionization potentials of olefins are similar to those of



arenes, and that olefins with large ΔIP (> 0.5 eV) undergo 1,2-addition reactions.

The symmetry-allowed 1,3-addition to benzene (S_1) is apparently the most efficient mode with the following olefins; cis and trans-2-butene,³⁶ cycloalkene,³⁵ isobutene, 2-methyl-2-butene,³⁵ vinyl acetate,³⁵ etc. The stereochemistry of the ethylene is preserved in the product. However, the relative amounts of the exo and endo isomers depend on the ethylene, although the endo isomer predominates in many cases.

1,3-Addition has been extended to a number of systems involving single alkenes and substituted benzenoid compounds. Their addition patterns and yields are listed in Table 2.

The "forbidden" 1,2-cycloaddition of ethylenes to singlet arenes seems to occur readily in those systems having marked donor-acceptor character.³⁵ Earlier findings that simple ethylenes yield only 1,2-adducts with the strong acceptor

Table 2. Photocycloaddition of various substituted arenes to olefins.

Substituents	position	Φ	olefines	ref
H	meta	0.16	c-C5 ^a	e
Me	1,3	0.21	c-C5	e
p-Me,i-Pr	3,5/2,6	(5:1)	c-C8 ^b	f
o-,m-,p-Xylene	1,3	.13/.05/.08	c-C5	e
OMe	1,3 (2,6)		c-C8 (c-C5)	f
o-,m-,p-Me,OMe	2,6		C5/OEt ^c /C8	g,h,f
CN	2,4/1,2	(2:1)	Cl ^d	i
F	2,5			j
p-F,Alkyl	2,6		c-C5	k
m-OMe,F	2,6		OEt	h

^a cyclopentene. ^b cis-cyclooctene. ^c vinyl ethyl ether.

^d cis-1,2-dichloroethene. ^e J. Cornelisse, et.al. J. Am.

Chem. Soc., 95, 6197 (1973). ^f A. Gilbert, et. al., J. Chem.

Soc., Perkin I, 1314 (1980). ^g T. R. Hoyer, Tetra. Lett., 22,

2523 (1981). ^h J. Cornelisse, Tetra. Lett., 23, 3827 (1982).

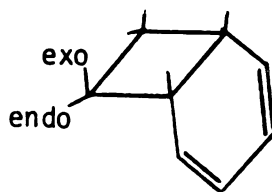
ⁱ A. Gilbert, et. al., J. Chem. Soc., Chem. Comm., 750 (1983).

^j D. Bryce-Smith, et. al., J. Chem. Soc., Chem. Comm., 112

(1980). ^k J. Cornlisse, et. al., Tetra. Lett., 26, 1893

(1985).

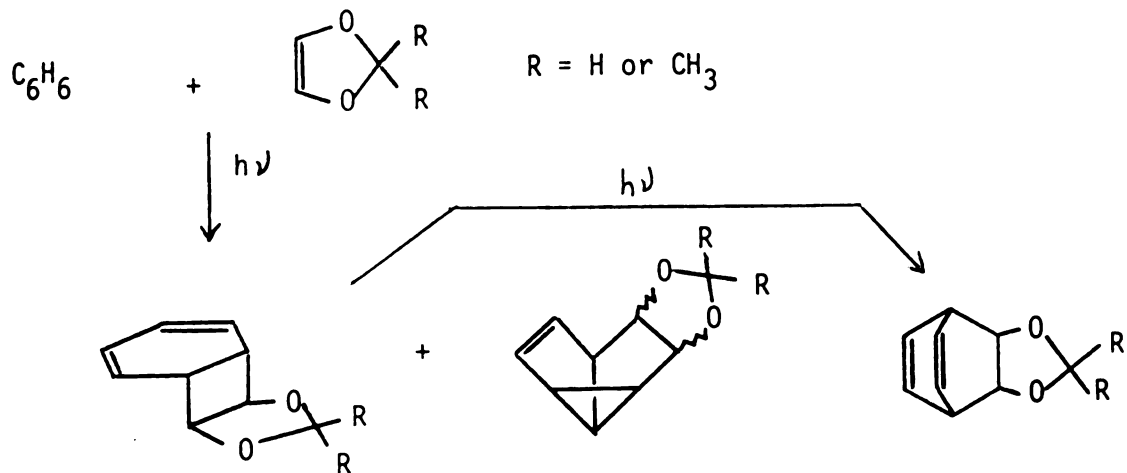
benzonitrile³⁷ also accord with the donor-acceptor rule. 1,2-Photocycloaddition to benzene is a major process with the donor ethylenes dihydropyran,³⁸ dimethoxyethenes,³⁹ tetramethylethylene,³⁹ and ethyl vinyl ether.³⁹ With the acceptor ethylenes (maleic anhydride,⁴⁰ acrylonitrile,⁴¹ etc.), 1,2-cycloaddition is the only process on irradiation of benzene.



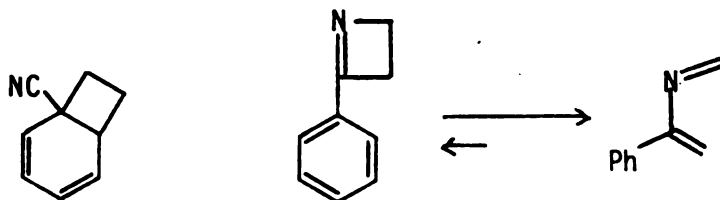
The 1,2-photoaddition of ethylenes to benzene leads to either exo or endo stereoisomers. The dienophilic ethylenes, maleic anhydride,⁴⁰ maleimide,⁴² and acrylonitrile⁴³ gave exo isomers, whereas the endo compound can be obtained from cis-2-butene³⁶ and cis-cyclooctene.⁴⁴ But methyl acrylate and methyl methacrylate gave a mixture of exo and endo isomer in the ratio of 2 : 1.⁴⁵ In general, exo-1,2-adduct are formed exclusively with the electron-rich alkenes, but electron-poor olefins give a mixture of two isomers.⁴⁶

Scharf and coworkers have examined the mechanism of the cycloaddition by studying benzene-cyclic vinyl ether system. 1,4-Dioxene gave mainly 1,2-adduct with benzene, but 1,3-dioxoles yielded 1,2- and 1,3-adduct together with 1,4-adducts that are shown to be derived in a secondary photoreaction for the 1,2-adducts.⁴⁷ Also their exciplex emission was reported for the first time in such benzene-alkene systems.⁴⁸

Photocycloaddition of benzonitrile with alkenes occurs at both nitrile group and the ring. The products are 1,2-adducts at 1 and 2 position of the ring and azetines.^{37,49}



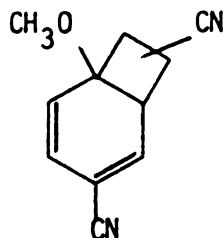
Cantrell⁵⁰ further studied the reaction of benzonitrile with various ethylenes. It was observed that with electron rich ethylenes (four alkyl, two alkoxy, two alkyl and one alkoxy substituent) the main product was 2-azabutadiene. With less electron-rich olefins, 1,2-photoaddition occurs to the ring: for example, 2-methyl-2-butene in benzonitrile yielded 62 % of



a mixture of adducts ($\Phi = 0.17$). Both types of ethylenes were observed to quench the arene fluorescence, from which observation it was deduced that the excited nitrile singlet is involved in the reactions.

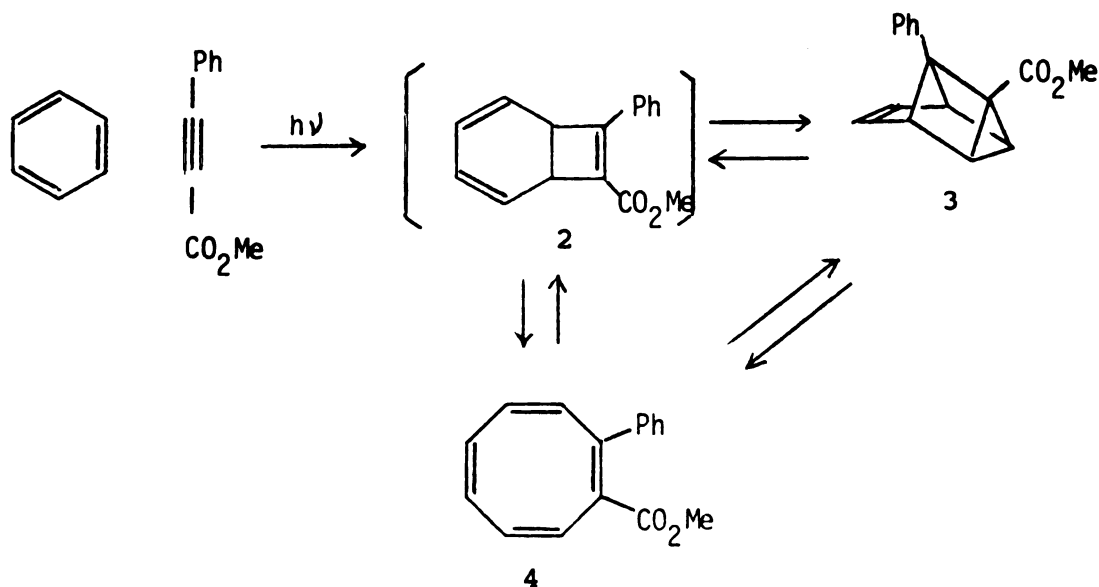
Methoxy-substituted benzonitriles were further studied. Irradiation of 4-methoxybenzonitrile in acrylonitrile⁵¹ yielded two 1,2-adducts (1,2 or 2,1-position to the methoxy

group) and an azacyclooctetraene which was originated from photoaddition of a nitrile function of acrylonitrile to the aromatic ring. The same benzonitrile in ethyl vinyl ether with 254 nm gave two 1,2-cycloadducts, but with cis-cyclooctene the 1,3-cycloadduct was the sole product. With cyclopentene both



3 and 4-cyanoanisole gave 1,3-photoadducts.⁵²

The photoaddition of acetylene to benzene ring yielded cyclooctatrienes via initial 1,2-addition.⁵³ Methyl phenylpropiolate and benzene were reported to give 1-carboxy-methyl-8-phenylcyclooctatetraene when irradiated at 254 nm or at wavelengths >290 nm, where only the acetylene absorbs light to a significant degree.⁵⁴ Further study⁵⁵ revealed that irradiation of a dilute solution of methyl phenylpropiolate in benzene at wavelengths longer than 290 nm leads to the formation of the tetracyclic compound:



With 254 nm, irradiation gave a 13 : 7 ratio of 3 and the cyclooctatetraene, 4, respectively and these two product could be interconverted photochemically or thermally. The authors suggested that the reaction occurs by way of the 1,2-cycloadduct (2, not isolated) and the lifetime of this is long enough for it to absorb a second photon in competition with the residual acetylene in the direct irradiation and cyclize to 3. It could not be clearly understood whether the conversion from 2 to 4 is a photochemical process or thermal isomerization. This reaction was further generalized: methyl t-buthylacetylene carboxylate in benzene gave also 5-t-buthyl-4-methoxycarbonyl derivative of 3 with cyclooctatetraenes (1.5 : 1 ratio).⁵⁶

The study of the effect of solvent polarity on various photocycloaddition reactions of ethylenes and acetylenes to benzene showed that the 1,3-addition has little sensitivity to solvent polarity change, but the 1,2-addition was dramatically influenced by alteration in the polarity.⁵⁷

In some intramolecular systems, where arenes and olefins are connected, the addition pattern and the efficiency of the reaction are dependent on the chain length and the type of chains linking addends. 5-Phenylpent-1-ene gave 2,6- and 1,3-addition products in a quantum yield of 0.11 and 0.045, respectively, and 6-phenylhex-1-ene reacted only at 1,3-position with a quantum yield of <0.005:⁵⁸ Both cis- and trans-6-phenylhex-2-enes gave meta-cycloadducts, the 1,3-product from the former and the 2,6-product from the latter isomer:⁵⁹

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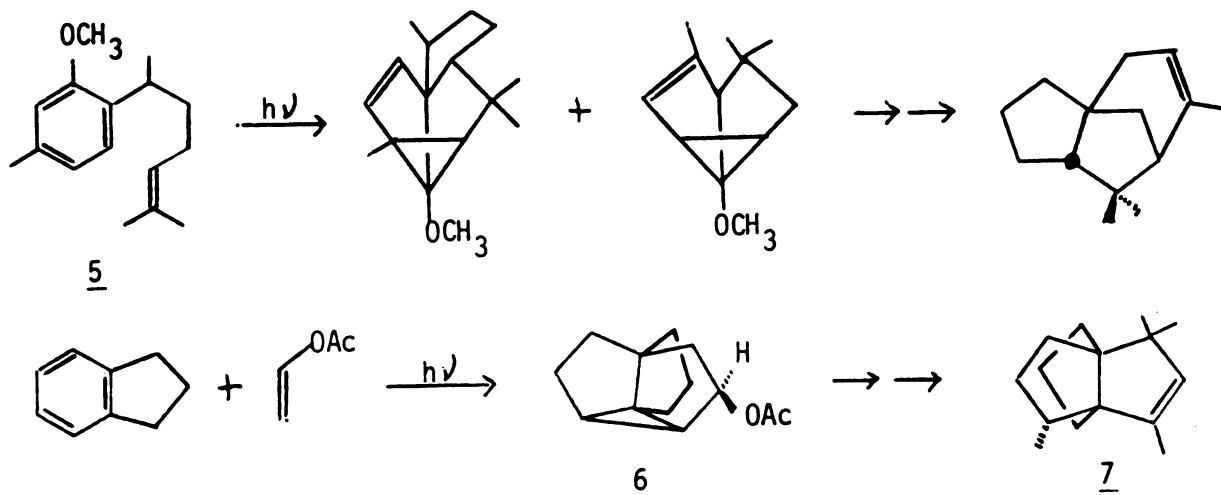
Table 3. Intramolecular cycloaddition of arenes to olefins.

compounds	orientation	Φ	ref
$\text{Ph}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$	2,6/1,3	.11/.041	59
$\text{Ph}-(\text{CH}_2)_3-\text{CMe}=\text{CH}_2$	1,3/2,6	.037/.023	60
$\text{Ph}-(\text{CH}_2)_3-\text{CMe}=\text{CMe}_2$	1,3/2,5/2,4	.013/.011/.006	60
$\underline{\text{c}}\text{-Ph}-(\text{CH}_2)_3-\text{CH}=\text{CHMe}$	1,3/isom	.26/.011	61
$\text{Ph-O}-(\text{CH}_2)_2-\text{CH}=\text{CH}_2$	2,4	not measurable	58
$\text{Ph-CH}_2\text{-O-CH}_2-\text{CH}=\text{CH}_2$	1,3/2,6	.052/.017	58
$\text{Ph}-(\text{CH}_2)_2\text{-O-CH}=\text{CH}_2$	2,5/1,3	.23/.006	58
$\text{Ph}-(\text{CH}_2)_3\text{-O-CH}=\text{CH}_2$	2,4/1,3	.05/.01	58
$\underline{\text{o}}\text{-MePh}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$	1,3/1,4	.51/.09	60
$\underline{\text{m}}\text{-MePh}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$	1,3/1,5	.024/.043	60
$\underline{\text{p}}\text{-MePh}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$	2,6	.06	60
$\underline{\text{o}}\text{-MeOPh}-(\text{CH}_2)_3-\text{CH}=\text{CH}_2$	1,3	.50	60
$\text{C}_6\text{F}_5\text{-OCH}_2-\text{CH}=\text{CH}_2$	1,2	not determined	62
$\text{Ph}-(\text{CH}_2)_3-\text{C}\equiv\text{CH}$	1,2		63

Phenylethyl vinyl ether underwent 2,5-addition, but 3-phenylpropyl vinyl ether gave 1,3- and 2,4-adducts. More results are summarized in Table 3. In general, meta addition is dominant in the intramolecular photocycloaddition between singlet arenes and olefins.

This 1,3-photoaddition was applied in the synthesis of several naturally occurring compounds by Wender and co-workers

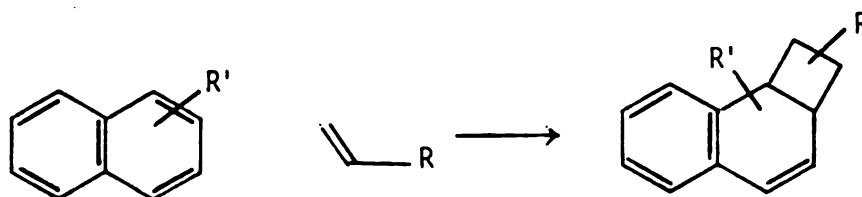
either intramolecularly or intermolecularly.⁶⁴ For examples, they reported on the synthesis of ($\pm$)- α -cedrene in three steps from the ethenyl-aryl bichromophoric system, 5^{64a} and have shown that the separated product 6 from irradiation of indane and vinyl acetate was converted into ($\pm$)-modhephene, 7, in an overall yield of 8.2 % in a total of six further steps.^{64e}



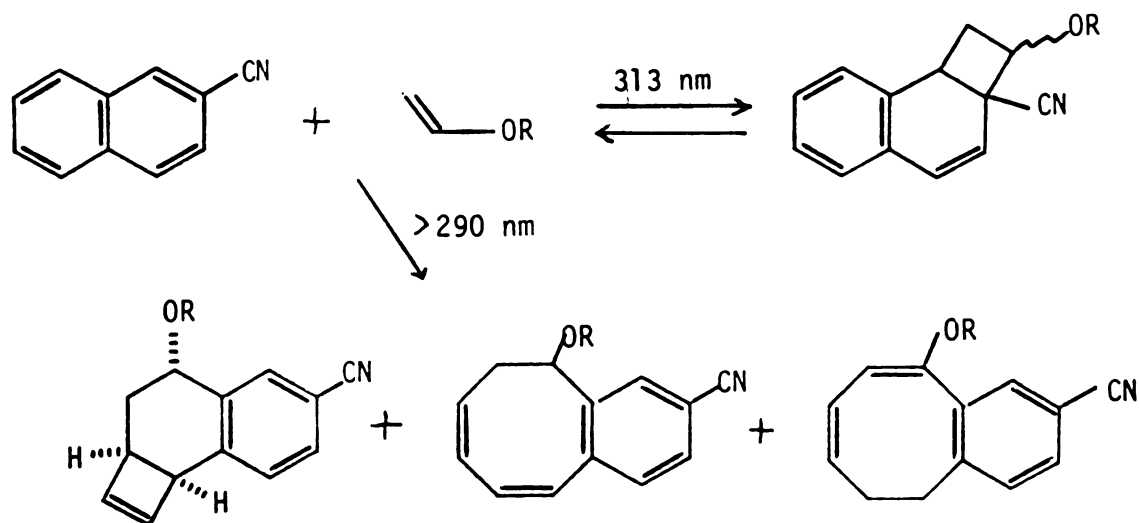
Gilbert et. al. reported that neither $\text{Ph-OCH}_2\text{CH}_2\text{CH=CH}_2$ nor $p\text{-CH}_3\text{CO-Ph-(CH}_2)_3\text{CH=CH}_2$ gives significant yields of cycloadducts upon irradiation.⁶¹ They focused on the singlet reaction with high energy (254 nm), even though the latter has strong absorption at around 290 nm. In this thesis, intramolecular quenching efficiencies and photocycloaddition of alkenoxyphenyl alkyl ketones will be studied.

It is interesting that a system with a nitrile group on either naphthalene rings or olefins undergoes efficient 1,2-photocycloaddition just like the benzene systems: acrylonitrile adds to 1,2-position of naphthalene upon irradiation.⁶⁵ Naphthalenes substituted by other than nitrile also underwent the photocycloaddition to olefins. Irradiation of 1-

or 2-naphthol or their trimethyl silyl derivatives with acrylonitrile yielded 1,2-adducts:⁶⁶



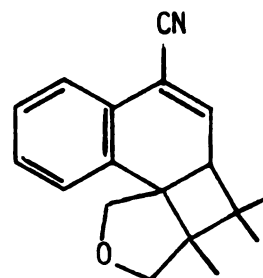
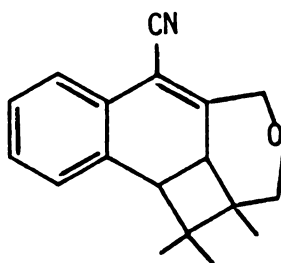
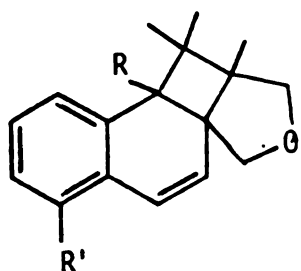
Irradiation of 1-cyanonaphthalene with methyl vinyl ether or phenyl vinyl ether gave mainly 1,2-adducts.⁶⁷ However, 2-cyanonaphthalene with alkyl vinyl ether showed a different type of photoreaction; products were 1,2-adducts, ring-expanded products, and cyclobutene products:⁶⁸



Upon 313 nm irradiation, only the [2 + 2] cycloadduct was observed. However, irradiation through Pyrex (>290 nm) afforded a cyclobutene as a main product. The 1,2-cycloadduct was assumed to be the precursor for the cyclooctatrienes and the cyclobutene formation. More details are presented in the above figure.

The intramolecular version of the cycloaddition of naphthalenes has been studied by McCullough et.al.⁶⁹ Later, it was found that neither $\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ nor $\text{CH}_2\text{CH}_2\text{OCH}=\text{CH}_2$ chain gives 1,2-adducts, only the olefinic chain of $\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$ undergoes the 1,2-addition.⁷⁰ The authors claimed that both intermolecular⁷¹ and intramolecular adduct come from the singlet exciplexes. Solvent effects⁷² and lifetime measurements of the exciplex emission⁷³ in this system were studied.

It is interesting to note here that the $-\text{CH}_2\text{OCH}_2-$ link between the chromophores has also been shown to be a particularly successful intervening unit for dianthryl



$\text{R} = \text{CN or H}$

$\text{R}' = \text{H or CN}$

compounds,⁷⁴ but not for phenyl vinyl systems.⁷⁵ Also, surprisingly, there are just few examples of the triplet cycloaddition,^{76,77} even though there are many examples of the photocycloaddition of the singlet or singlet exciplexes.

Kinetics - The triplet lifetime of the ketones in this thesis was measured by the Stern-Volmer quenching technique. 2,5-Dimethyl-2,4-hexadiene was used to quench the triplet ketones by energy transfer. The mathematic expression of this

$$\begin{aligned}\Phi_o &= \Phi_{isc} k_H \tau_T \\ \Phi &= \Phi_{isc} \frac{k_H}{1/\tau_T + k_q [Q]} \\ \Phi_o/\Phi &= 1 + k_q \tau_T [Q] \quad \text{----- Equation (1)}\end{aligned}$$

where Φ_o, Φ = quantum yield in the absence and the presence of a quencher, respectively

$\tau_T = 1/\Sigma k_i$, triplet lifetime

k_q ; rate constant for quenching by the diene

k_H ; rate constant for the product formation

$[Q]$; concentration of a quencher

process is given in Equation (1).

A plot of Φ_o/Φ vs. $[Q]$ gives a straight line with an intercept of 1 and a slope of $k_q \tau_T$. The quenching rate of 2,5-dimethyl-2,4-hexadiene is usually close to the rate of diffusion in a given solvent. The values for k_q are known to be equal to $10 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ in acetonitrile⁷⁸ and $5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ in benzene at 25 °C.⁷⁹ Thus the triplet lifetime can be calculated from the slope of the Stern-Volmer plot.

Research goal - In this thesis, the chain-length effect on intramolecular charge transfer quenching of alkenoxyphenyl ketones (π, π^* lowest triplets) and α -benzoyl- ω -alkanes (n, π^* triplets) by their olefinic moieties will be explained. For the former, the triplet-cycloaddition will be discussed in quantitative sense (triplet lifetime measurement, intramolecular quenching efficiencies of the olefinic moieties, the

mechanism for the cycloadduct formation). This is the first triplet-state cycloaddition study, as far as we know.

RESULTS

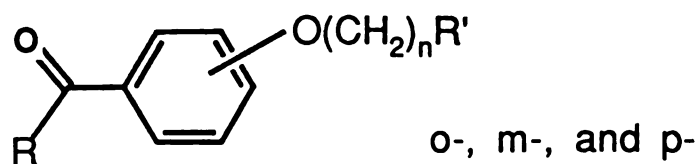
A. Alkenoxyphenyl Ketones

The alkenoxyphenyl ketones were made by the S_N2 reaction between the phenolates of the hydroxyphenyl ketones and the corresponding alkenyl halides. For the para and meta ketones, anhydrous potassium carbonate in dry acetone was good enough to generate the phenolates from the phenols, but for the ortho ketones more basic condition (sodium metal in ethanol) was used for the same purpose.

1. Photocycloaddition and Identification of Photoproducts

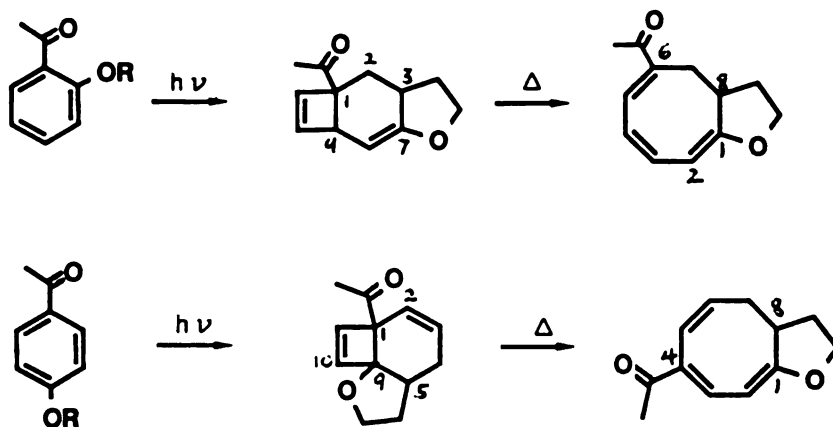
a. General - 0.01 to 0.02 M argon-bubbled benzene solution of various alkenoxyphenyl alkyl ketones were irradiated at 313 nm or above 295 nm (Pyrex glass filter). After >90% conversion (from the GC check), the solvent was evaporated below 30 °C, and the products were identified as 1-acyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-dienes (from the ortho ketones) or 1-acyl-8-oxatricyclo[7.2.0.0^{5,7}]undec-2,10-dienes (from the para ketones). The cycloadducts collected by preparative GC (injection port; 190-200 °C, oven; 160-190 °C, detection port; 200-210 °C; helium gas; 65 ml/min) were identified as 7- and/or 8-alkyl-substituted 4-acyl-11-oxabicyclo[6.3.0]undec-1,3,5-trienes (from the para ketones)

Scheme III



	<u>R</u>	<u>R'</u>	
AP _n 1	CH ₃	-CH=CH ₂	n = 1,2,3,4,9.
AP _n 2	CH ₃	-C(CH ₃)=CH ₂	n = 1,2.
AP _n cis	CH ₃	cis-CH=CH ₂ Et	n = 2,3.
AP _n 3	CH ₃	-CH=C(CH ₃) ₂	n = 1,2,3.
VP _n 1	n-Bu	-CH=CH ₂	n = 1,2,3,4,9.
VP _n 2	n-Bu	-C(CH ₃)=CH ₂	n = 1,2.
VP _n cis	n-Bu	cis-CH=CH ₂ Et	n = 2,3.
VP _n 3	n-Bu	-CH=C(CH ₃) ₂	n = 1,2,3.

or 6-acyl-11-oxabicyclo[6.3.0]undec-1,3,5-trienes (from the ortho ketones). The homodecoupling technique in ^1H -NMR was mainly used for the identification of products.

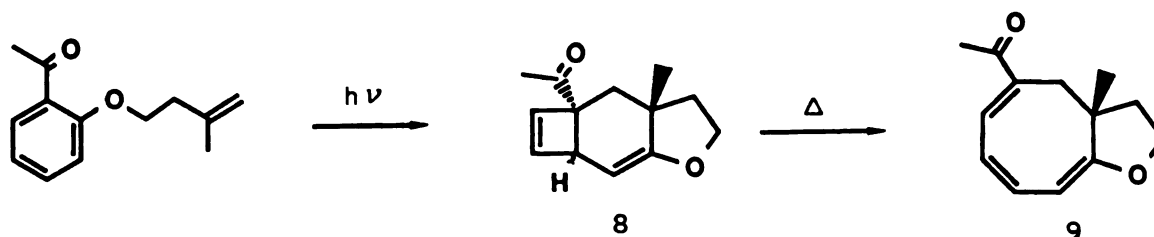


The type II products were synthesized separately in most cases and their retention times were compared on the GC or HPLC. Or they were collected by preparative GC and identified from the ^1H -NMR spectra.

The ortho alkenoxyphenyl ketones undergo more efficient photoaddition than the para derivatives and all adducts could be derived from the 1,2-addition between ipso and ortho carbons of the phenyl ring and vinyl carbons.

b. Photoproducts from o-VP₂2 and o-AP₂2 - Irradiation of 0.5-1.0 gr of o-(3-methyl-3-buten-1-oxy)valerophenone, o-VP₂2, or o-(3-methyl-3-buten-1-oxy)acetophenone, o-AP₂2, in benzene at either > 295 nm or 313 nm gave the type II product (minor from the o-VP₂2) and two other photoproducts. From the intensity of ^1H -NMR signals, the ratio of the two new products

was about 7:1. The major photoproduct of α -VP₂ was identified as 1-valeryl-3-methyl-6-oxatricyclo[7.2.0.0^{1,9}]undec-7,10-diene. The minor product was not identified and after 1-2 weeks in a refrigerator it disappeared from the ¹H-NMR spectrum.

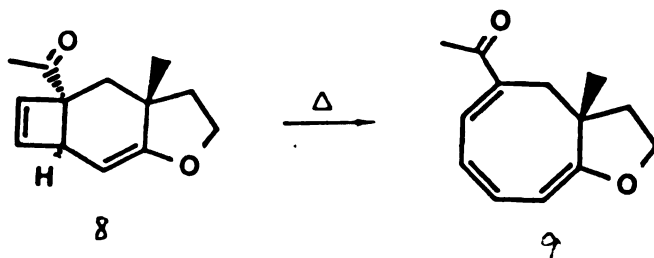


The product, **8**, which showed the same molecular ion peak as that of the starting ketone in the mass spectrum, has the following spectroscopic data: two peaks at δ 6.04 and 5.81 (H-11 and H-10) coupled to each other with $J = 2.8$ Hz. This is a characteristic coupling pattern of the vinyl protons in a cyclobutene.⁸⁰ At δ 4.98 (H-8), there is another vinyl proton, which couples with the proton at δ 3.32 (H-9), $J = 6.6$ Hz. The proton at 3.32 ppm couples with one of the cyclobutene protons (H-11 at 6.04 ppm) with $J = 0.9$ Hz and can be assigned as a bridgehead proton of a bicyclo[4.2.0]octa-2,7-diene. The multiplet at 3.85-3.75 ppm was assigned to two hydrogens at C-5 and indicated a rigid 5-membered ring. All the above couplings were confirmed by the homodecoupling technique (Fig. 2). Also the ¹³C-NMR spectrum supports this structure; there are two double bonds. One is a typical enol ether double bond,⁸⁰ i.e., 163.9 (s, C-8) and 90.8 (d, C-7) ppm. Another double bond (C-10, C-11) appears at 144.8 (d) and 139.6 (d) ppm (Fig. 3). The carbonyl carbon appears at 207.9 ppm. The nuclear

Overhauser effect (NOE) showed about a 5 % increment of the H-11 peak when the methyl at C-3 was irradiated, but no enhancement (< 2%) was observed in the peaks of H-9, H-10, and acetyl protons; therefore the methyl group at C-3 and the cyclobutene ring should be in the cis-position and the carbonyl group in the trans-position. The UV-Visible spectrum shows no major absorption above 250 nm, except for a weak 295 nm absorption ($\epsilon = 200$). The IR spectrum confirms that a carbonyl group is present.

The major difference between the products from α -AP₂2 and α -VP₂2 is in their ¹H-NMR spectra. In the ¹H-NMR spectrum of the latter, two protons on the α -carbon next to the carbonyl group show a clear ABX splitting pattern ($J = 17.1, 7.1$ Hz), which reflects the restriction in bond rotation between the carbonyl carbon and the α -carbon.

The rearranged products, **2**, from a preparative GC or a column chromatograph were acylcyclooctatrienes which were identified mainly by the UV-Visible spectrum and homodecoupling of the ¹H-NMR spectrum. In the case of 3-acetyl-1-methyl-9-oxabicyclo[6.3.0]undec-3,5,7-triene, the UV-Visible spectrum shows a λ_{max} at 374 nm ($\epsilon = 4400$) and 237 nm ($\epsilon = 19000$) in hexane.



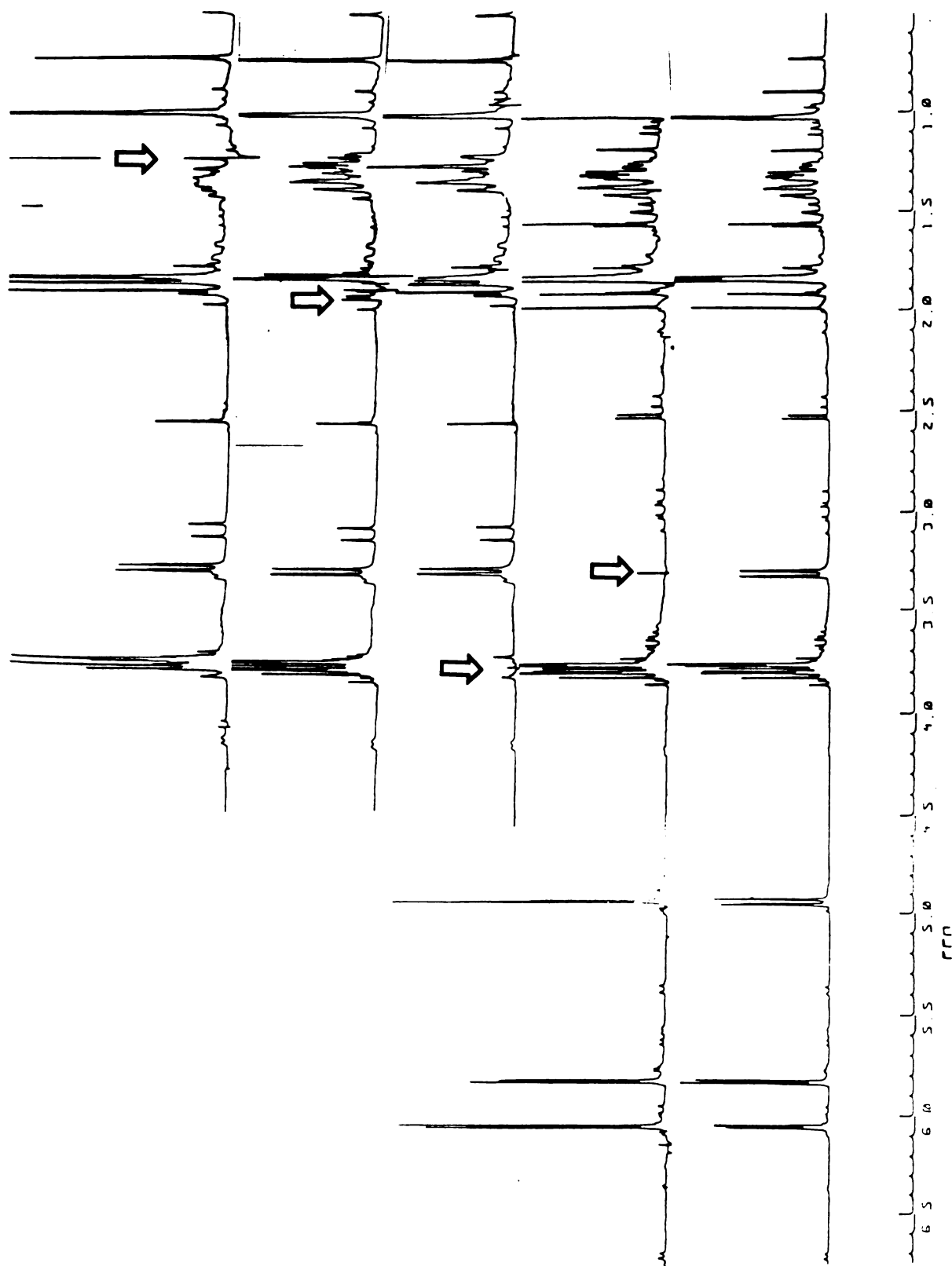


Figure 2. Homodecoupling of ^1H -NMR spectra of 1-acetyl-3-methyl-6-oxatricyclo-[7.2.0.0^{1,9}]undeca-7,10-diene (C_6D_6 , 250 MHz)

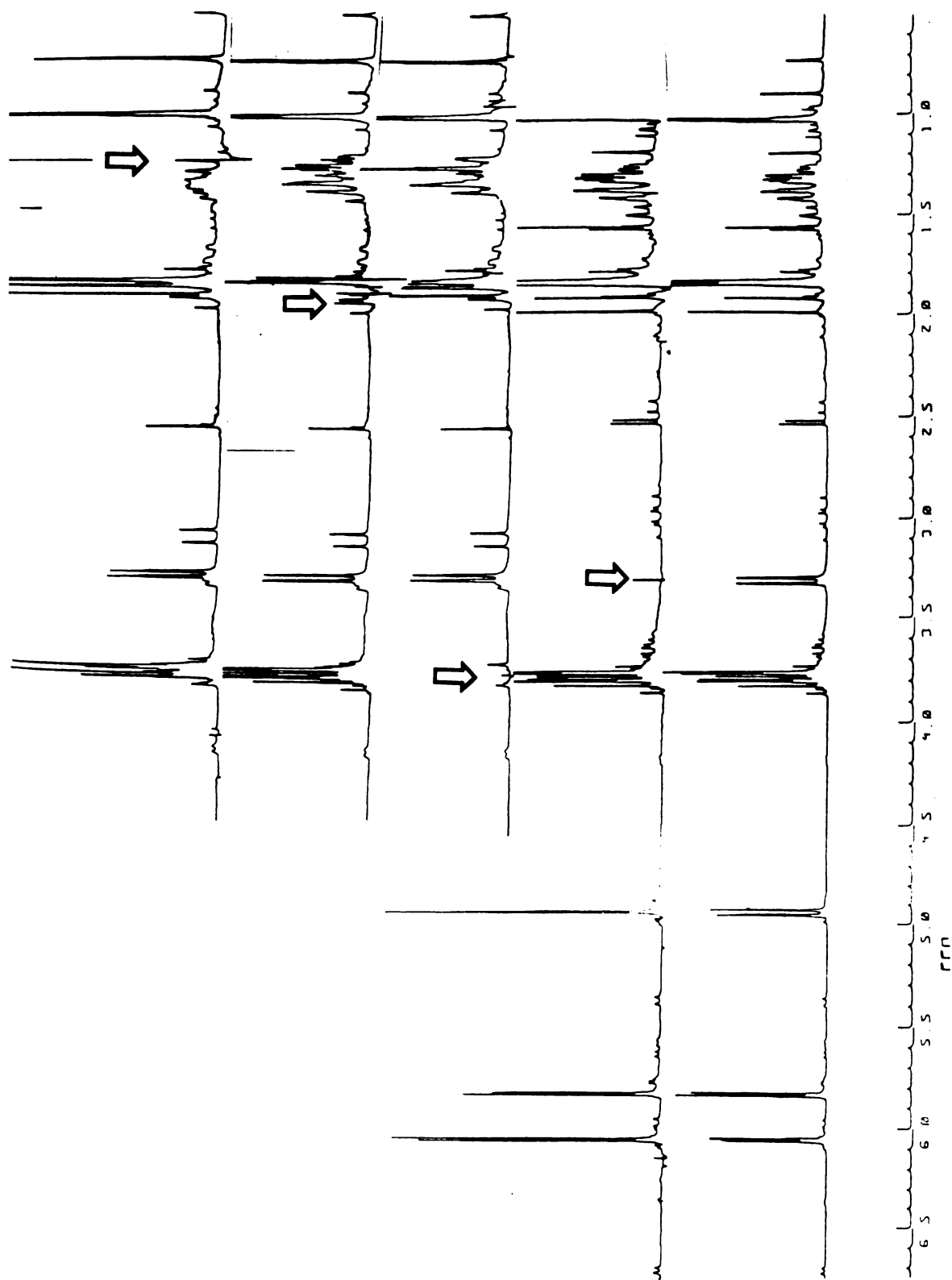


Figure 2. Homodecoupling of ^1H -NMR spectra of 1-acetyl-3-methyl-6-oxatricyclo-[7.2.0.0.1.9]undeca-7,10-diene (C_6D_6 , 250 MHz)

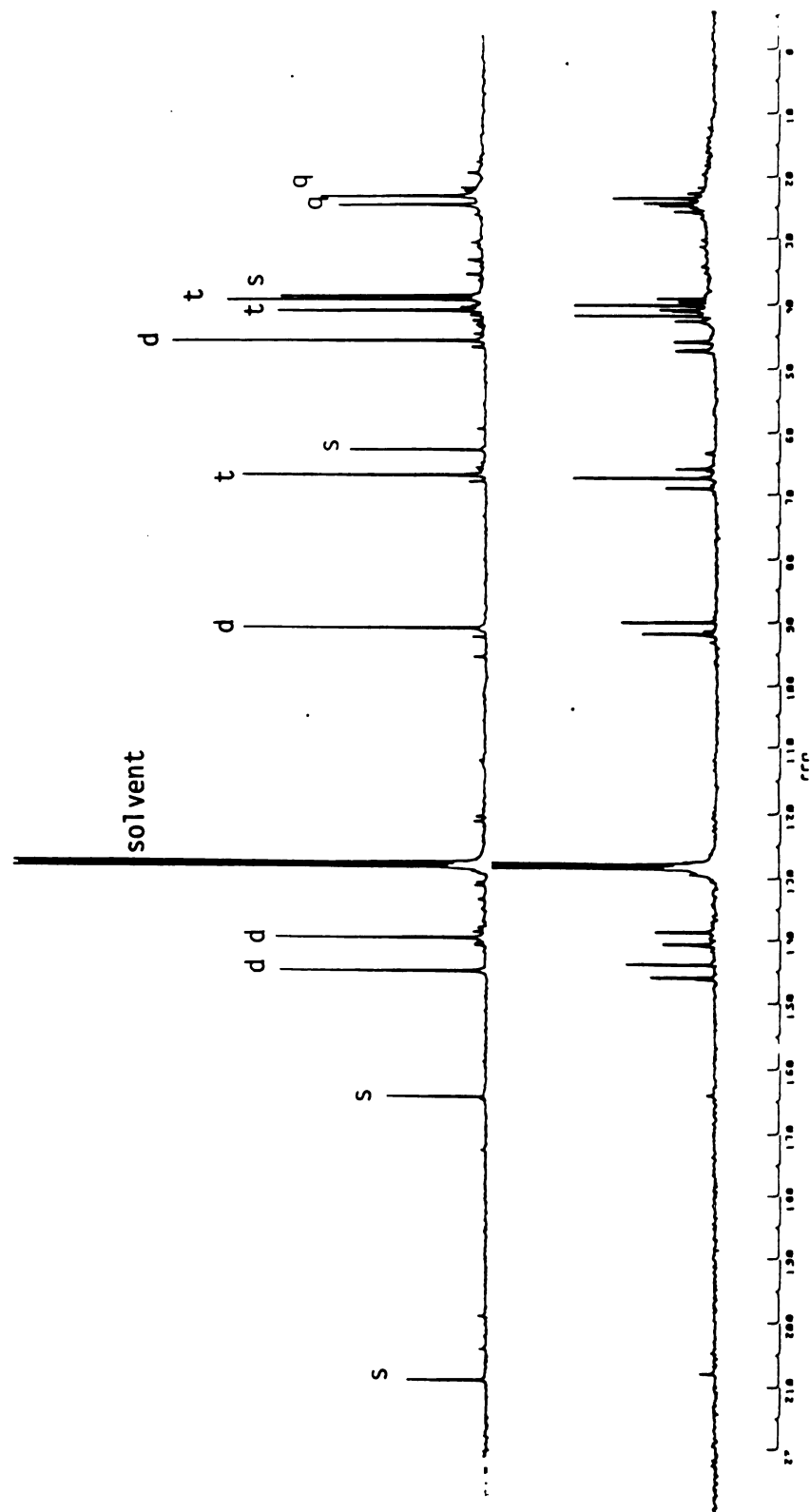


Figure 3. The ^{13}C -NMR spectra of 1-acetyl-3-methyl-6-oxatricyclo[7.2.0.01,9]undeca-7,10-diene in C_6D_6 .

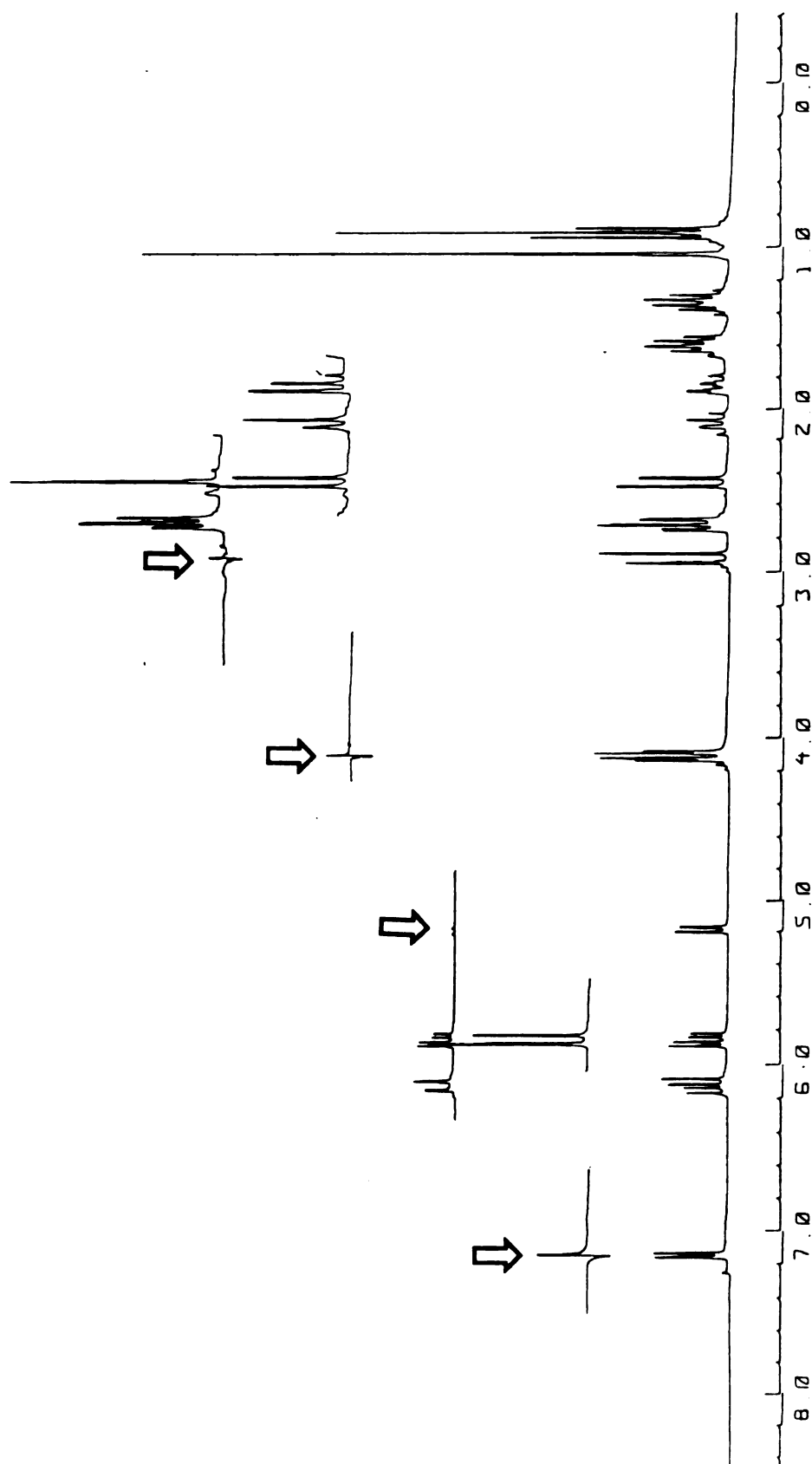


Figure 4. Homodecoupling of ^1H -NMR spectra of 1-methyl-3-valeryl-9-oxabicyclo[6.3.0]undeca-3,5,7-triene in CDCl_3 .

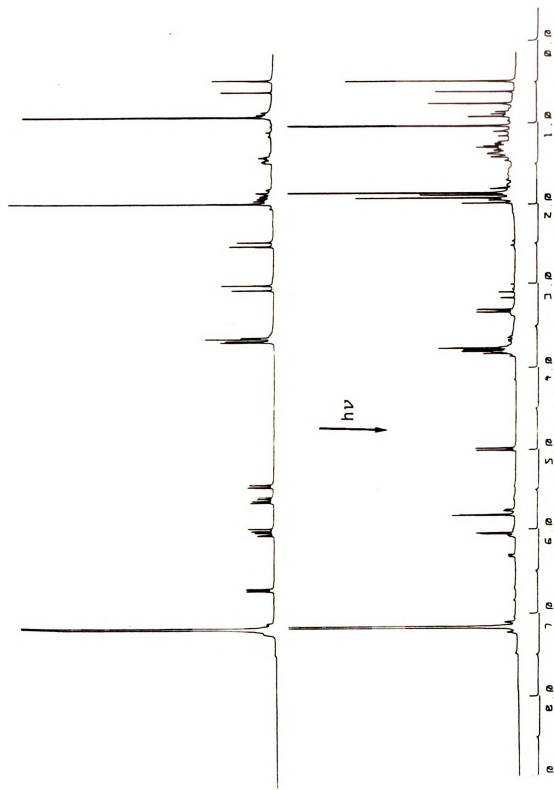
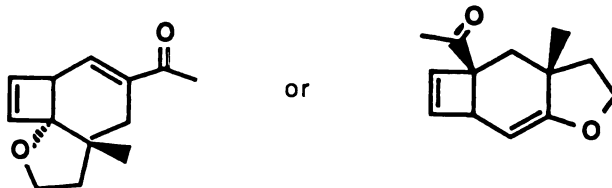


Figure 5. Irradiation of 1-methyl-3-acetyl-9-oxabicyclo[6.3.0]undeca-3,5,7-triene in C_6D_6 at 313 or 365 nm; the bottom spectrum is the same as that of the photoproduct of $q-AP_{22}$.

In the ^1H -NMR spectrum, there are four vinyl protons; two coupled doublets at 7.13 (H-4, $J = 5.7$ Hz) and 5.17 ppm (H-7, $J = 7.7$ Hz) and two doublet of doublets at 6.12 (H-6, $J = 7.7$, 12.5 Hz) and 7.7 ppm (H-5, $J = 12.5$, 5.7 Hz). Two doublets at 2.91 and 2.45 ppm couple each other ($J = 13.2$ Hz) and are considered to be the methylene protons (C-2) of the 8-membered ring (Fig. 4).

Irradiation of **9** in argon-bubbled benzene- d_6 (about 3-4 mg in 0.4 ml) at 313 nm or 365 nm gave the original mixture of two components, **8** and an unknown product, (the same ratio, 7:1), which was confirmed by the ^1H -NMR spectra (Fig. 5). From the interconversion, the unknown products is expected to be an isomer of **8**; possibly a diastereomer or one by different ring closure.

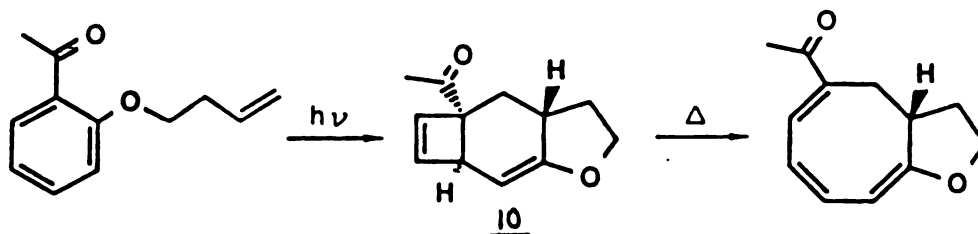


c. Products from $\text{q-VP}_2\text{1}$ and $\text{q-AP}_2\text{1}$ - Irradiation of $\text{q-(3-buten-1-oxy)acetophenone}$, $\text{q-AP}_2\text{1}$, or $\text{q-(3-buten-1-oxy)-velerophenone}$, $\text{q-VP}_2\text{1}$, (0.5-1.0 gr in 250 ml benzene with argon bubbling) at >295 nm (Pyrex filter) gave 1-acetyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-diene, **10**, (and the type II product, $\text{q-AP}_2\text{1}$, from the $\text{q-VP}_2\text{1}$). Unlike $\text{q-AP}_2\text{2}$, the ^1H -NMR study showed that the starting ketone could not be completely converted to the cycloadduct; i.e., the starting ketone disappeared continuously, but the product peaks did not grow

up after a certain level. From this, it was assumed that the photoproduct is not very stable photochemically.

Again from the ^1H -NMR spectrum of the product, the cyclobutene ring was identified; two doublets at 5.86 and 5.78 ppm (H-10, H-11) split each other with $J = 2.8$ Hz. The doublet at 4.96 ppm (H-8) splits the doublet at 3.26 ppm with $J = 6.6$ Hz and those came from an enol ether doublet. Two multiplets at 3.78 and 3.50 ppm split each other ($J = 8.5$ Hz) and also with some other protons, and assigned as two protons next to the oxygen of a rigid 5-membered ring.

The product collected from a preparative GC was 3-acetyl-9-oxabicyclo[6.3.0]undec-3,5,7-triene. This octatriene also was not perfectly pure in the ^1H -NMR spectrum and assumed to be not very stable at the oven temperature (170 – 180°C). ^1H -NMR spectrum tells that there are four vinyl protons which show two doublets with moderate J coupling constants (H-4, δ 7.13, $J = 6.2$ Hz; H-7, δ 5.35, $J = 8.8$ Hz) and two doublet of doublets with another big J coupling constant (H-5, δ 5.75, $J = 13.0$, 6.2 Hz; H-6, δ 6.06, $J = 13.0$, 8.8 Hz). Actually H-7 has a doublet of doublet with an additional small coupling ($J = 1.9$ Hz) to the proton at 3.04 ppm (H-1, d of d, $J = 13.4$,



1.9 Hz). All the above assignments were confirmed also by the homodecoupling of the spectra.

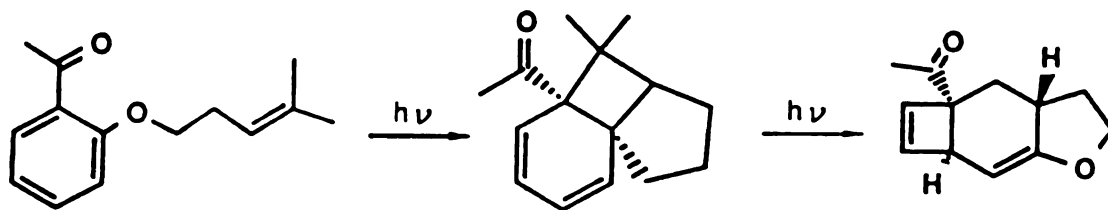
d. Products from o-AP₂cis - Irradiation of o-(cis-3-hexen-1-oxy)acetophenone (0.5-1.0 gr in 250 ml benzene with argon bubbling) at >295 nm (Pyrex filter) yielded two products in a ratio of 4:1 from the ¹H-NMR integration. The cyclobutene derivative was a minor product in this case. The major product showed two vinyl protons, one with a J value of 5.1 Hz at 6.32 ppm and another with a small coupling constant (J = 0.9 Hz at 6.00 ppm), but was not identified. After column chromatography, this product turned into a cyclooctatriene, which has four vinyl protons (two doublet of doublets, two doublets).

e. Products from o-AP₂3 - The initial photoproduct (40-50 % conversion) of o-(4-methyl-3-penten-1-oxy)acetophenone, o-AP₂3, (0.5-1.0 gr in 250 ml benzene with argon bubbling at >295 nm of a Pyrex filter) showed four vinyl protons in the ¹H-NMR spectrum. A further purified mixture from column chromatography contained less than 20 % of the starting ketone and was a colorless liquid. This product was deduced to be 3-acetyl-2,2-dimethyl-9-oxatricyclo[6.3.0.0^{3,8}]undec-8,10-diene from the following data (¹H-NMR and the decoupling): two vinyl doublets at 5.43 and 5.34 ppm (H-4, H-7) with J coupling constants of 9.6 and 9.8 Hz, and two doublet of doublets at 5.69 and 5.53 ppm (H-5, H-6) with J = 9.6, 5.6 Hz and J = 9.8, 5.6 Hz, respectively. These are typical values for vinyl coupling constants in a cyclohexene rings.⁸⁰ The possibility for cyclooctatriene (four vinyl protons) formation was excluded; it has no visible color and its vinyl protons have different δ values from those of the

other cyclooctatrienes. If it was a cyclooctatriene, these doublets should have smaller coupling constants (6-7 Hz), because each doublet proton and their neighboring protons cannot be located on the same double bond or the same plane.

Prolonged irradiation of the mixture of the starting ketone and the cyclohexadiene gave 1-acetyl-2,2-dimethyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-diene. Two vinyl protons of the cyclobutene appeared as doublets at 6.00 and 5.76 ppm with $J = 2.8$ Hz (H-10, H-11). Another vinyl proton (H-8, 4.97 ppm, d of d, $J = 2.7, 6.4$ Hz) split the peak at 3.54 ppm (H-9, d, $J = 6.4$ Hz) and the peak at 2.35 ppm (H-3, d of t, $J = 2.7, 10.1$ Hz) (see Fig. 6).

1-Acetyl-2,2-dimethyl-6-oxatricyclo [7.2.0.0^{3,7}]undec-7,10-diene (direct photoproducts from α -AP₂3) was converted to 1-acetyl-2,2-dimethyl-6-oxatricyclo[5.4.0.0^{3,7}]undec-8,10-diene on heating at 130 °C for 30-40 min. Also a little of the starting ketone, α -AP₂3, was detected.



f. Products from the substituted α -AP₂ derivatives - 2'-(3-Methyl-3-buten-1-oxy)-5'-methylacetophenone gave one product upon irradiation (313 nm) in benzene with the same molecular ion peak with the starting ketone. The ¹H-NMR spectrum of the photoproduct showed one peak at 5.49 ppm ($J =$

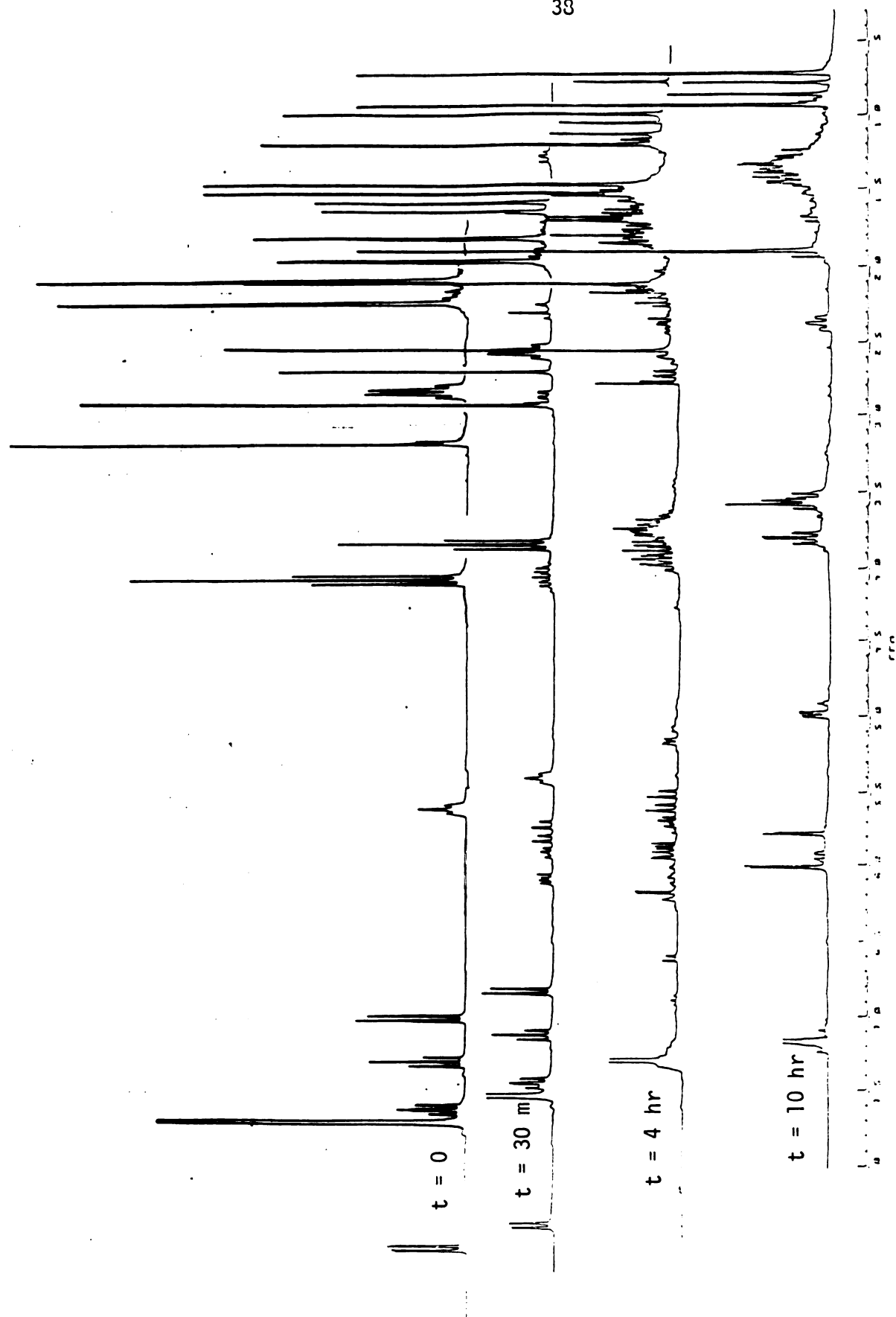


Figure 6. The ^1H -NMR spectra of $q\text{-AP}_{23}$ as a function of time of 313 nm irradiation in C_6D_6 .

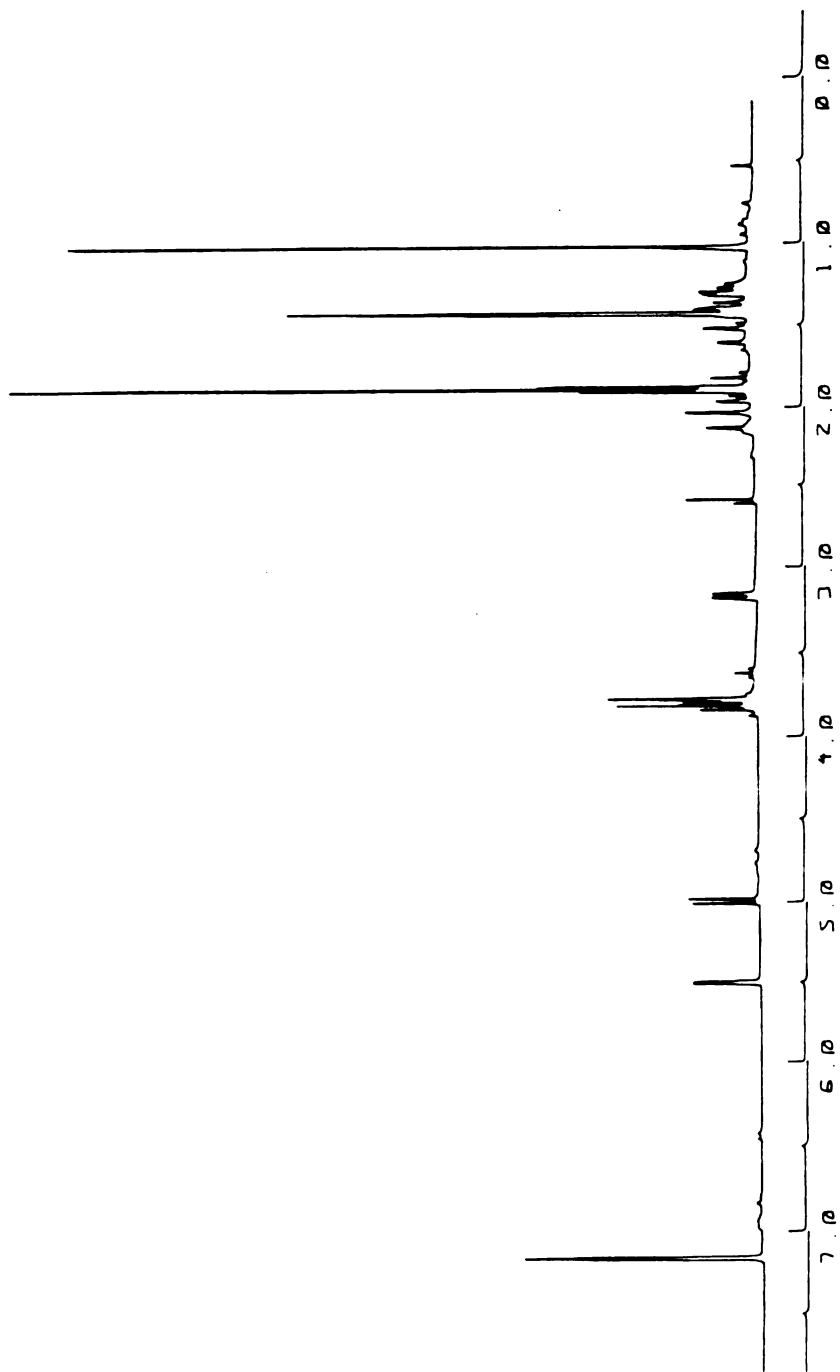
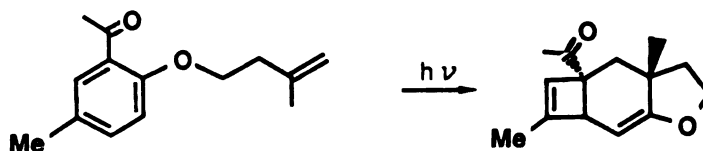


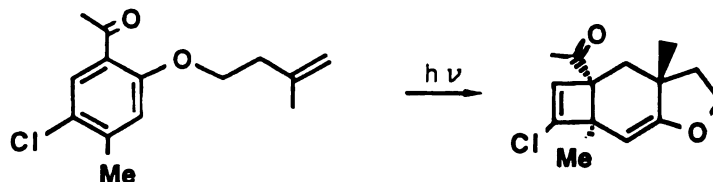
Figure 7. The ^1H -NMR spectrum of the photoproduct of 2'-(3-methyl-3-buten-1-oxy)-5'-methylacetophenone (C_6D_6 , 250 MHz).

1.5 Hz) where two doublets of cyclobutene ($J = 2.8$ Hz) appear when there is no 5'-methyl group (product from α -AP₂2). Also, as usual, H-8 and H-9 appear at 4.99 and 3.16 ppm with $J = 6.7$ Hz, respectively. Two protons of C-5 are shown at 3.78 ppm as a multiplet. Three singlet peaks of methyl groups come at 1.88, 1.42, and 1.01 ppm and identified as the methyl of the acetyl group, that on the vinyl carbon (C-10), and that on C-3, respectively. Unlike α -AP₂2, there was no minor product detected (see Fig. 7).



Irradiation of 2'-(3-methyl-3-buten-1-oxy)-5'-chloro-4'-methylacetophenone (less than 100 mg in argon-bubbled benzene in a test tube) gave one product, whose growth was monitored on a GC. This product showed the same molecular ion peak with the starting ketone ($M^+ = 254/252$ (1/3)). On the $^1\text{H-NMR}$ spectrum of the photoproduct, two vinyl singlets at 6.71 and 5.15 ppm replaced the two doublets that appeared when there were no 5'-chloro and no 4'-methyl. Another unusual two doublets were shown at 2.98 and 2.25 ppm ($J = 13.1$ Hz). Also two ABX-type peaks were observed at 1.99 and 1.26 ppm ($J = 12.9$ Hz). Three methyl group singlets appeared at 1.91, 1.80, and 0.87 ppm. UV-Visible spectrum of the product did not show major absorption at around 350 nm. From these data, this

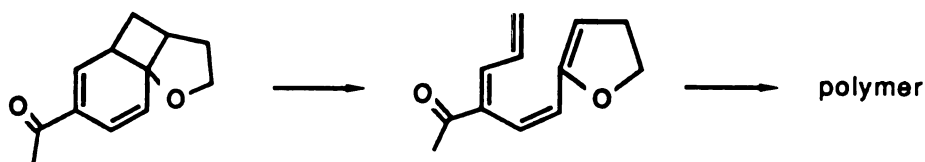
product was assigned again as a cyclobutene, i.e., 1-acetyl-10-chloro-3,9-dimethyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-diene.



Tables 4 and 5 contain some of the chemical shifts and coupling constants of the cyclobutene products and the cyclo-octatrienes of the ortho-alkenoxycyclohexenyl ketones, respectively.

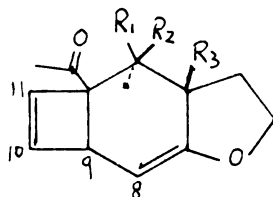
g. Products from the para-alkenoxycyclohexenyl ketones -

The para-alkenoxycyclohexenyl ketones gave 1-acyl-8-oxatricyclo[7.2.0.0^{5,9}]undec-2,10-dienes as products, which thermally rearranged to 4-acyl-11-oxabicyclo[6.3.0]undec-1,3,5-trienes on a preparative GC. Unlike the ortho derivatives, irradiation



of para ketones gave colloidal precipitates in the solutions. These were assumed to come from the polymerization of the tetraenes which could be formed by the ring opening of 1,2-adducts.

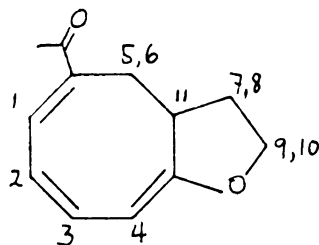
Table 4. Selected chemical shift values and coupling constants of the products of ortho-alkenoxyphe~~n~~yl ketones in benzene-d₆. (250 MHz)



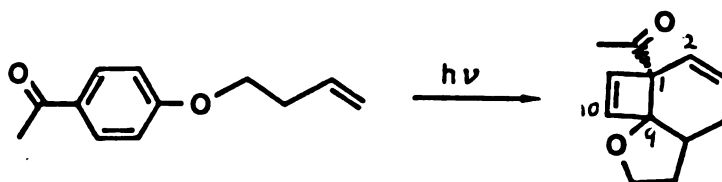
	<u>R₁=R₂=R₃=H</u>		<u>R₃=Me</u>		<u>R₁=Et</u>		<u>R₁=R₂=Me</u>	
	δ	J	δ	J	δ	J	δ	J
H-11	5.78	2.8	5.81	2.8	5.89	2.9	5.74	2.8
H-10	5.86	2.8	6.04	2.8	6.04	2.9	5.99	2.8
H-9	3.26	6.6	3.32	6.6	3.52		3.54	6.4
H-8	4.96	6.6	4.98	6.6	4.92		4.98	6.4

TABLE 5. Chemical shift and coupling constants of the cyclootatrienes from *o*-alkenoxyphenyl ketones in CDCl_3 .

from <i>o</i> -butenoxyphenyl ketone					<i>o</i> -(3-methyl-3-butenoxy)				
	ppm		J, Hz			ppm		J, Hz	
H-1	7.13	d	1H	$J_{1,2} = 6.2$		7.13	d	1H	$J_{1,2} = 5.7$
H-2	5.75	d,d	1H	$J_{1,2} = 6.2$		5.84	d,d	1H	$J_{1,2} = 5.7$
				$J_{2,3} = 13.0$					$J_{2,3} = 12.8$
H-3	6.06	d,d	1H	$J_{2,3} = 13.0$		6.12	d,d	1H	$J_{2,3} = 12.8$
				$J_{3,4} = 8.8$					$J_{7,4} = 7.7$
H-4	5.34	d,d	1H	$J_{3,4} = 8.8$		5.17	d	1H	$J_{3,4} = 7.7$
				$J_{4,5} = 1.9$					
H-5	3.04	d,d	1H	$J_{4,5} = 1.9$		2.91	d	1H	$J_{5,6} = 13.2$
				$J_{5,6} = 13.4$					
H-6	2.23	d,d	1H	$J_{5,6} = 13.4$		2.45	d	1H	$J_{5,6} = 13.2$
				$J_{6,11} = 8.3$					
H-7	1.85	m	1H	$J_{7,9} = 8.1$		2.08	t,d	1H	$J_{(9,10)} = 10.4$
H-8						1.85	t,d	1H	$J_{(9,10)} = 3.2$
H-9	4.13	d,t	1H	$J = 2.5, 8.1$		4.10	d,d	2H	$J = 3.2$
H-10	4.02	d,t	1H	$J = 5.7, 11.5$					
H-11	2.73	m	1H	$J = 8.3$					



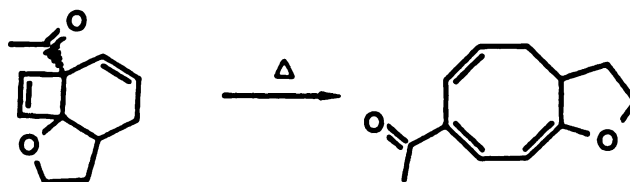
h. Products from p-VP₂1 and p-AP₂1 - Both p-(3-buten-1-oxy)acetophenone and its valerophenone derivative gave one photoproduct with either 313 nm or > 295 nm (Pyrex) of light in benzene (ca. 0.05 M). The valerophenone derivative gave the type II product additionally. The new product from the acetophenone derivative was identified as 1-acetyl-8-oxatricyclo [7.2.0.0^{5,9}]undec-2,10-diene by its ¹H-NMR, ¹³C-NMR, GC-MS, IR spectra. The molecular ion peak of the product is 190 (m/e) which is the same as that of the starting ketone. Four vinyl protons were observed in the NMR spectra; three of them were doublets and one was a multiplet. Two doublets at 6.06 and 5.85 ppm split each other with J = 2.7 Hz (H-10, H-11), which is very similar to that from the ortho derivatives. This strongly suggests the existence of a cyclobutene again. The other doublet at 5.83 ppm (H-2) and the multiplet at 5.59 ppm (H-3) split each other with J = 11.1 Hz. Two protons at 3.64 and 3.51 ppm split each other with J = 8.0 Hz and were identified as methylene protons next to the oxygen of a rigid



oxacyclopentane. The ¹³C-NMR spectrum showed a carbonyl carbon at 210.3 ppm and four olefinic carbons (C-2, C-3, C-10, C-11) at 139.0, 138.4, 126.3, and 125.8 ppm.

Two thermally rearranged products were collected from a preparative GC. Both showed the same molecular weight as that

of the starting ketone. The first product which had nearly the same retention time as that of the starting ketone on SE-30 column showed three vinyl protons in the ^1H -NMR spectrum; 7.12 (d, 1H, $J = 5.2$), 6.07 (d, 1H, $J = 12.6$), 5.93 (d of d, 1H, $J = 5.2, 12.6$) ppm. Unfortunately, the amount was too small and variable, and it was not further identified. The second product with a longer retention time was a yellow liquid and identified as 4-acetyl-11-oxabicyclo[6.3.0]undec-1,3,5-triene. Its ^1H -NMR spectrum showed four vinyl protons; two doublets at δ 7.00 and 5.40 (H-3 and H-2) coupled each other with $J = 6.8$ Hz, and the doublet (H-5) at 6.27 ppm was coupled with the multiplet (H-6) at 5.92 ppm ($J = 12.5$ Hz). H-8 appeared at 3.06 ppm as a multiplet and the singlet of the acetyl group came at 2.28 ppm. The details of the ^1H -NMR homodecoupling result are shown in Fig 8. The ^{13}C -NMR showed a carbonyl carbon at 199.3 ppm and six olefinic carbons at 170.5, 144.6, 137.8, 131.6, 125.1, and 96.1 ppm. The upfield peak at 96.1



ppm was assumed to be C-1, which is a usual chemical shift of an enol ether.⁷⁷

i. Products from p-VP₂ and p-AP₂ - p-(3-Methyl-3-butenoxy)acetophenone and its valerophenone also gave two thermally-rearranged products, one was identified as a

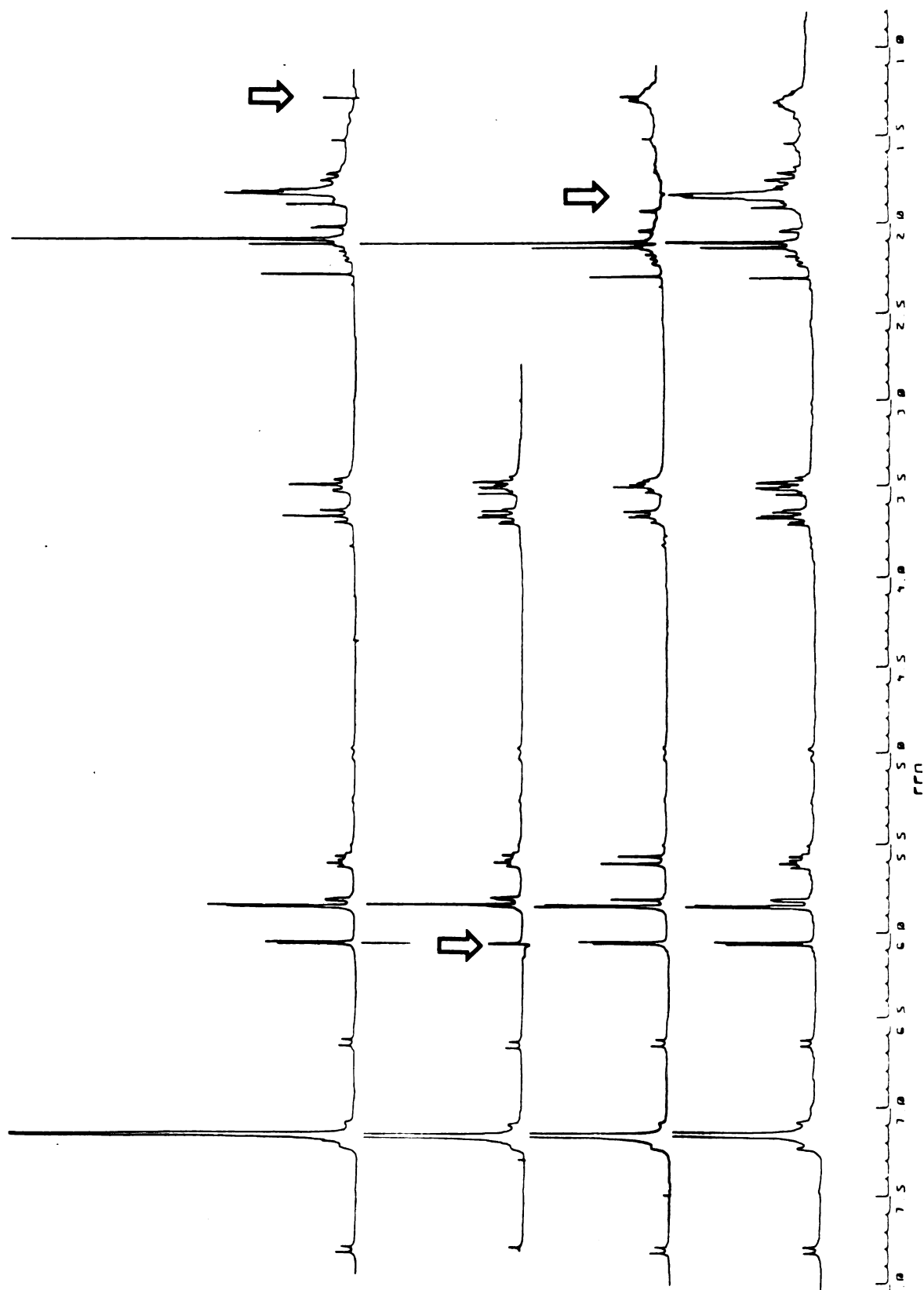


Figure 8. Homodecoupling of ^1H -NMR spectra of the photoproduct from pAP₂₁. (C_6D_6 , 250 MHz).

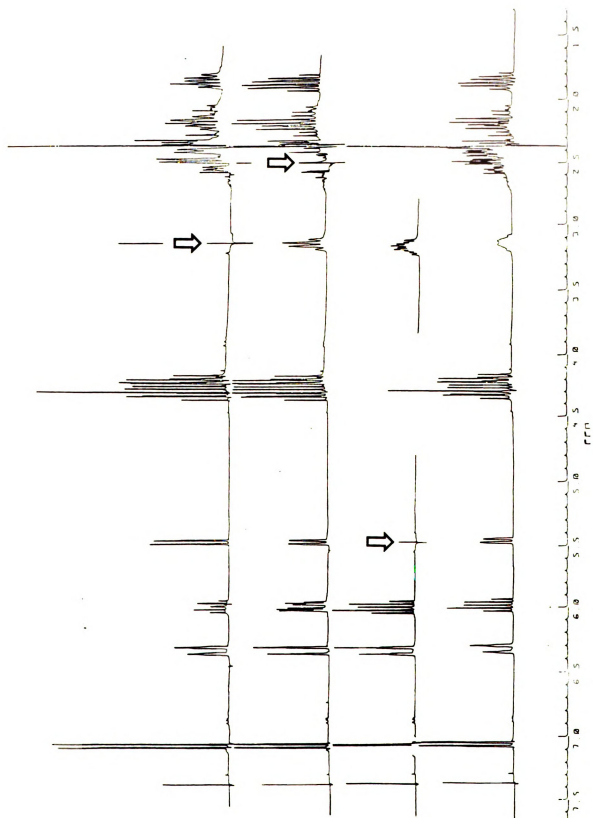


Figure 9. Homodecoupling of ^1H -NMR spectra of the thermally rearranged product from p-AP₂1 (CDCl_3 , 250 MHz).

cyclooctatriene which has four vinyl protons (three doublets, one multiplet). The other was not identified. But the products from the prep GC contained some other unidentified products, too.

j. Products from p-VP₂cis - Irradiation of p-(cis-3-hexen-1-oxy)valeropenone at 313 or >295 nm in benzene gave its trans derivative efficiently ($\Phi = 0.27$). p-(trans-3-hexen-1-oxy)valerophenone was identified mainly by the ¹H-NMR spectra. There were no change in the chemical shift of aromatic protons between two ketones; δ 7.92 (d, 2H), 6.91 (d, 2H). However, there is big difference in the coupling constants of the vinyl protons of the cis and trans ketone; 10.7 and 15.7 Hz, respectively (see Fig 10).⁸⁰ Allylic protons showed slightly different δ values. While two allylic methylenes of the cis ketone appeared at 2.51 and 2.11 ppm, those of the trans ketone were shown at 2.48 and 2.04 ppm. IR spectra and GC-MS spectra of the cis and trans ketones were almost identical and could not tell the differences between them. Higher conversion (6-10 hr irradiation in an immersion well with a Pyrex filter) gave an equilibrium mixture of more than 80 % of the trans derivative, which was monitored on a HPLC (100 % hexane, 1.2 ml/min, Ultrasphere Si column with an UV detector at 270 nm, the trans ketone comes out before the cis ketone). Prolonged irradiation gave a cycloadduct which has two vinyl protons of a cyclobutene and two more vinyl protons (Table 6).

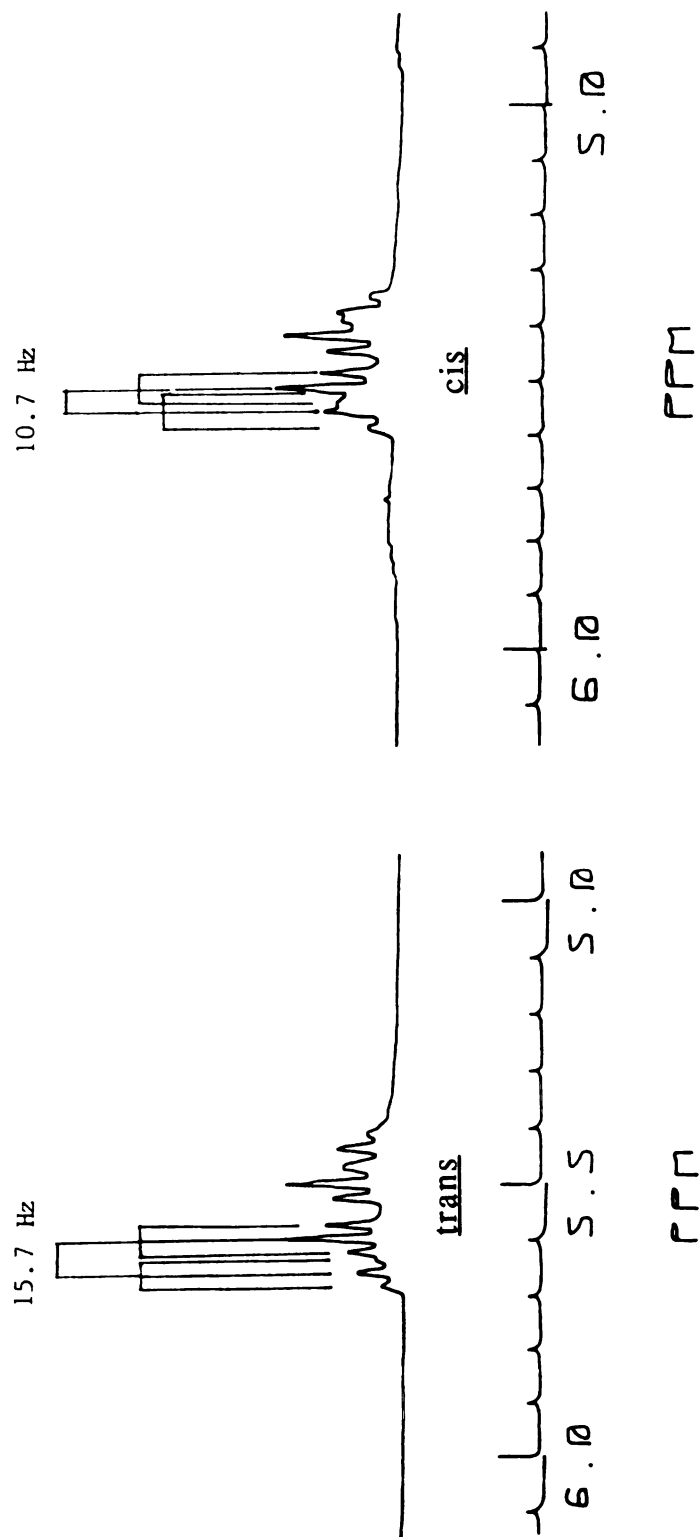
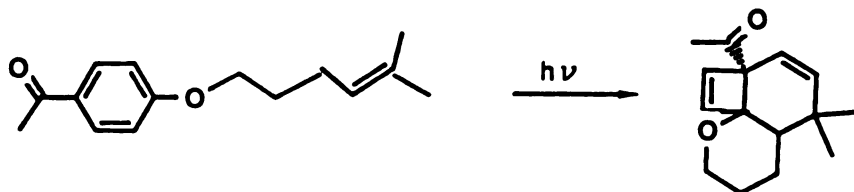


Figure 10. Coupling constants of vinyl protons of cis and trans-p-(3-hexen-1-oxy)valerophenone (C_6D_6 , 250 MHz).

k. Products from p-AP₂3 and p-AP₃3 - p-(4-Methyl-3-penten-1-oxy)phenyl ketones were inert upon irradiation. Seven days of irradiation gave one small new peak, but it was not identified. However, the irradiation of p-(5-methyl-4-hexen-1-oxy)acetophenone gave a product which have two protons (each doublets, $J = 3.1$ Hz) of a cyclobutene and another pair of vinyl protons (two doublets, $J = 10.2$ Hz). Upon further irradiation, four vinyl protons which are similar to those of cyclooctatrienes, were built up on the ^1H -NMR spectra (see Fig. 11).



1. Bimolecular Photocycloaddition - The product collected by preparative GC after irradiation of p-methoxyacetophenone in 1-hexene with 313 nm light, showed four vinyl protons; two doublets couple each other at 7.08 and 5.19 ppm ($J = 5.2$ Hz), other doublet at 5.67 ppm ($J = 12.3$ Hz), and a doublet of doublet at 5.82 ppm ($J = 12.3$ Hz). These J coupling patterns were similar to those of cyclooctatrienes and this product was considered as a cyclooctatriene derived from the bimolecular addition. Stereochemistry of the product was not determined completely, but from the doublet of doublet at 5.82 ppm, it was assumed that a 1-hexene was added to 3- and 4-position of the phenyl ring and also the n-butyl group of the

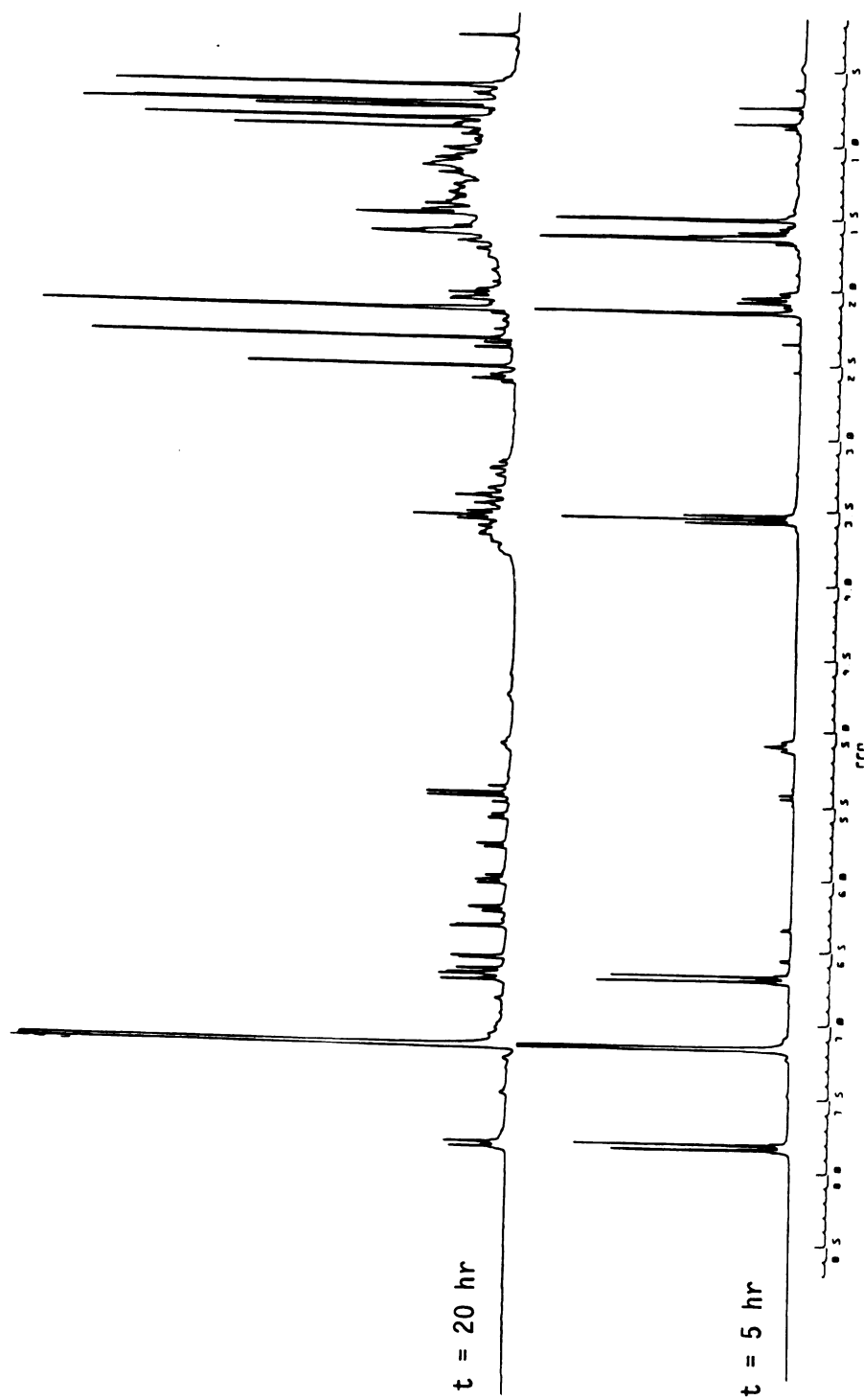


Figure 11. The ^1H -NMR spectra of Q-AP₃₃ as a function of time of 313 nm irradiation in C_6D_6 .

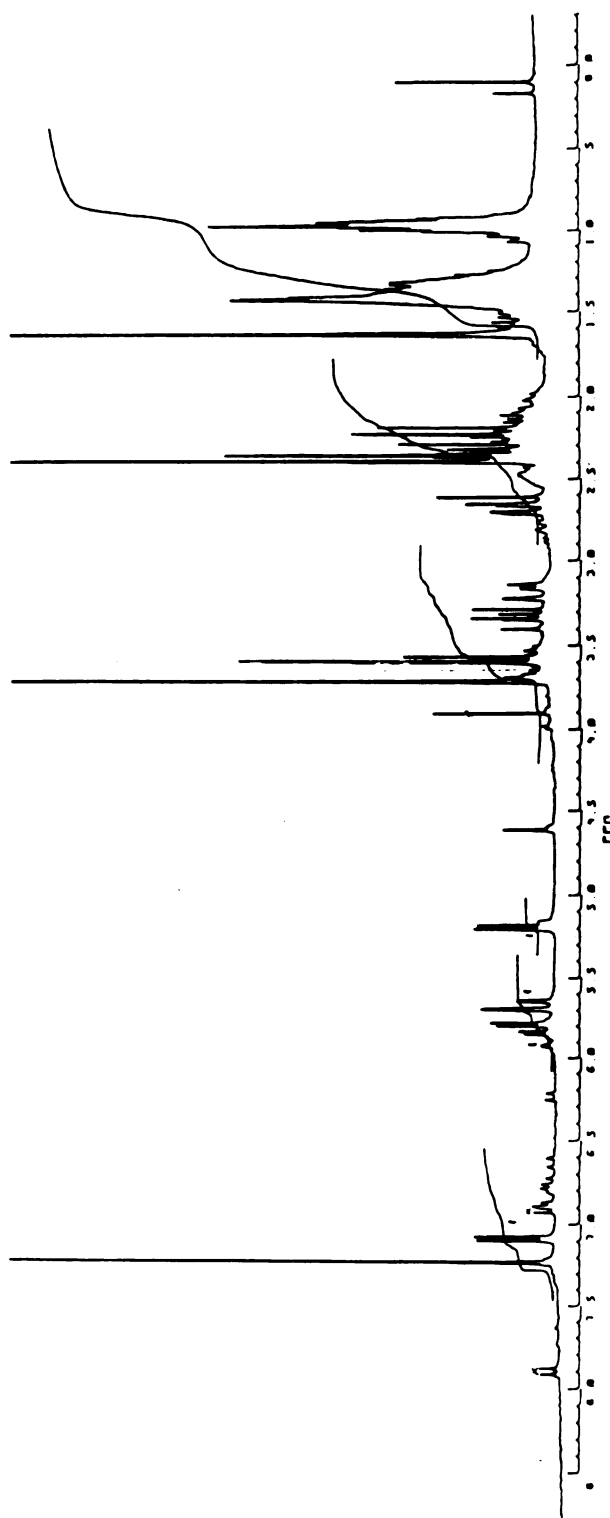
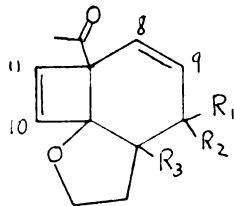


Figure 12. The ^1H -NMR spectrum of the cycloadduct from *p*-methoxyacetophenone and 1-hexene (CDCl_3 , 250 MHz).

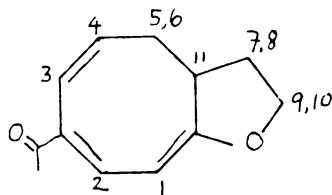
Table 6. Selected chemical shift values and coupling constants of the products of para-alkenoxyphenyl ketones in benzene- d_6 . (250 MHz)



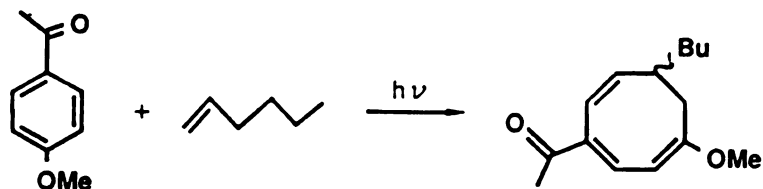
	$R_1=R_2=R_3=H$		$R_1=Et$		$R_1=R_2=Me$	
	δ	J	δ	J	δ	J
H-11	5.85	2.7	6.25		6.34	3.1
H-10	6.06	2.7	6.35		6.55	3.5
H-9	5.83	11.1			5.46	10.2
H-8	5.59	11.1			5.39	10.2

TABLE 7. Chemical shift and coupling constants of the
cyclooctatrienes from p-alkenoxyphenyl ketones
(250 MHz, CDCl₃).

From p-butenoxyphenyl ketone				p-pentenoxyphehyl ketone			
	ppm		coupling		ppm		coupling
H-1	5.40	d 1H	$J_{1,2} = 6.8$		5.58	d 1H	$J_{1,2} = 7.3$
H-2	7.00	d 1H	$J_{1,2} = 6.8$		6.90	d 1H	$J_{1,2} = 7.3$
H-3	6.27	d 1H	$J_{3,4} = 12.5$		5.35	d 1H	$J_{3,4} = 11.3$
H-4	5.92	q 1H	$J_{3,4} = 12.5$ $J_{4,5} = 6.8$		6.09	t,d 1H	$J_{3,4} = 11.3$ $J_{4,5} = 7.6$
H-5,6	2.29-2.50	m 2H	$J_{4,5} = 6.8$ $J_{5,6} = 6.3$				
H-7	1.83	m 1H	$J_{7,8} = 6.3$				
H-8	2.13	m 1H	$J_{7,8} = 6.3$				
H-9	4.16	m 1H	$J_{7,8} = 6.8$				
H-10	4.24	m 1H	$J_{7,8} = 6.8$				
H-11	3.06	m 1H	$J_{5,6} - J_{6,7} = 6.3$				

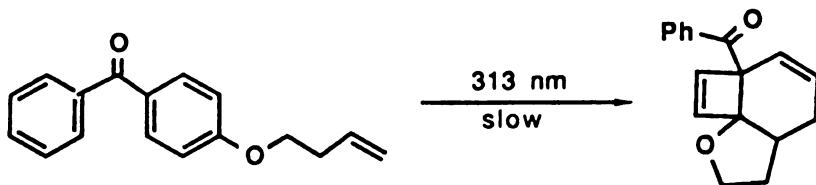


1-hexene was located away from the methoxy group. UV-Visible spectrum showed an absorption maximum at 312 nm (see Fig. 12).



m. Product from the benzophenone derivative -

Irradiation of p-(3-buten-1-oxy)benzophenone in argon-bubbled benzene-d₆ (ca. 0.05 M) at 313 nm for 48 hrs showed small amount of a product (< 2%) from the ¹H-NMR spectrum. The product had typical vinyl J-coupling of a cyclobutene in the spectra, but it was not further isolated.



2. Time-based ¹H-NMR and UV-Visible Spectra

To figure out possible intermediates, the time-based NMR and UV-Visible spectra of alkenoxyphenyl ketones were taken with 313 nm irradiation. UV-Visible spectra showed new peak at around 340-370 nm and assumed to come from the acyl-cyclooctatrienes. However, the ¹H-NMR spectra showed growing-up of the cycloutene products from the beginning.

Chronological UV-Visible spectra were recorded for *o*- and *p*-alkenoxyphenyl ketones in acetonitrile and benzene (10^{-4} - 10^{-5} M) which were irradiated at 313 nm. Generally, the intensity of the new peak at 340-370 nm depends very much on the position and the number of the alkyl substituents on the double bond. For the *o*-(3-buten-1-oxy)acetophenone and *o*-(3-methyl-3-buten-1-oxy)acetophenone, the intensity of new peaks around 370 nm was high and clearly the absorption maximum was observed (Fig. 15, 16). However, for *o*-(3-hexen-1-oxy)acetophenone and *o*-(4-methyl-3-penten-1-oxy)acetophenone, the intensity was weak and it was buried under a π, π^* peak of the starting ketone (Fig. 17, 18).

The UV-Visible spectra of *o*-AP₂2 (2.5×10^{-4} M in argon-bubbled acetonitrile or benzene in an UV cell) were taken with short time intervals. The spectra showed a quick decrease of π, π^* absorption and L_a band (305 and 245 nm, respectively) and a build-up of two new absorptions with 374 and 237 nm maxima. These two new absorption maxima are identical with those of 6-acetyl-8-methyl-11-oxabicyclo[6.3.0]undec-1,3,5-triene.

However, after 1-2 min irradiation, the 374 nm peak decreased slowly and eventually disappeared after ca. 15-20 min irradiation. The final spectrum was very similar to that of 1-acetyl-3-methyl-6-oxatricyclo[7.2.0^{3,7}.0]undec-7,10-diene.

Irradiation (313 nm) of 3-acetyl-1-methyl-9-oxabicyclo[6.3.0]undeca-3,5,7-triene, which was isolated from a prep GC by injecting the tricyclic photoproduct of *o*-AP₂2, showed a rapid decrease of the 374 nm absorption band in the UV-Visible

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spectrum. The final absorption spectrum was similar to that of 365 nm irradiation of the same cyclooctatriene and also similar to that of the cyclobutene product of o-AP₂2 (Fig. 19).

Time-based ¹H-NMR spectra were also taken for the ketone in argon-bubbled benzene-d₆ in a small test tube (every two hours). Irradiation (313 nm) of 0.1-0.05 M solution of o-AP₂2 gave the ¹H-NMR spectra corresponding to 1-acetyl-3-methyl-6-oxatricyclo[7.2.0^{3,7}.0]undec-7,10-diene from the beginning.

UV-Visible absorption spectra of o-(cis-3-hexen-1-oxy)acetophenone solution (1.4 x 10⁻⁴ M in argon-bubbled acetonitrile in an UV cell) with 313 nm irradiation also showed a new absorption peak at ca. 350 nm, which disappeared upon prolonged irradiation (15-20 min).

Time-based ¹H-NMR spectra of the same ketone, cis-o-AP₂2, (0.1-0.05 M in argon-bubbled benzene-d₆) showed the growing-up of the major unknown product and the cyclobutene from the beginning.

Irradiation of o-(4-methyl-3-penten-1-oxy)acetophenone (0.1-0.05 M in argon-bubbled benzene-d₆) showed the initial formation of the cyclohexadiene at 30-40 % conversion, but the cyclobutene product was the final photoproduct upon prolonged irradiation (ca. 6 hr) as confirmed by the ¹H-NMR spectra. In this case, the UV-Visible spectra also showed two new maxima at 283 and 273 nm which were assumed to come from the cyclohexadiene. Then, the intensity at 340-390 nm was increased slowly and it was much weaker than that of o-AP₂2.

Irradiation of p-(3-buten-1-oxy)acetophenone at higher concentration (0.1-0.05 M) led to the formation of the

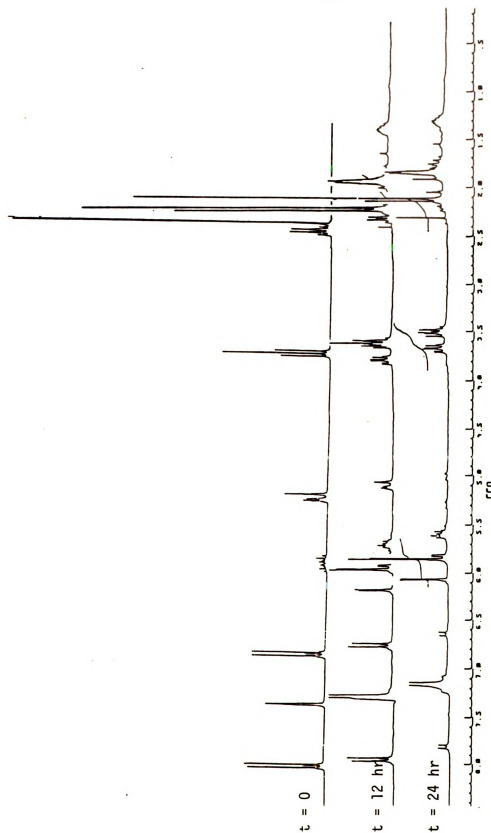


Figure 13. The ^1H -NMR spectra of $p\text{-AP}_21$ as a function time of 313 nm irradiation in C_6D_6 .

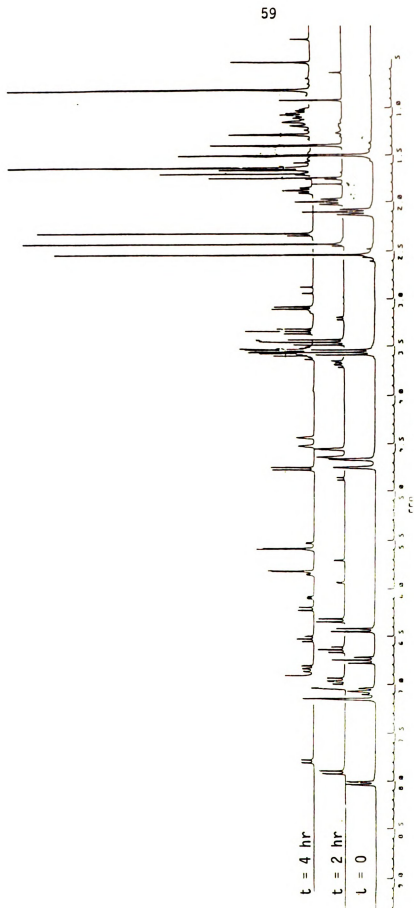


Figure 14. The ^1H -NMR spectra of $q\text{-AP}_{22}$ as a function of time of 313 nm irradiation in C_6D_6 .

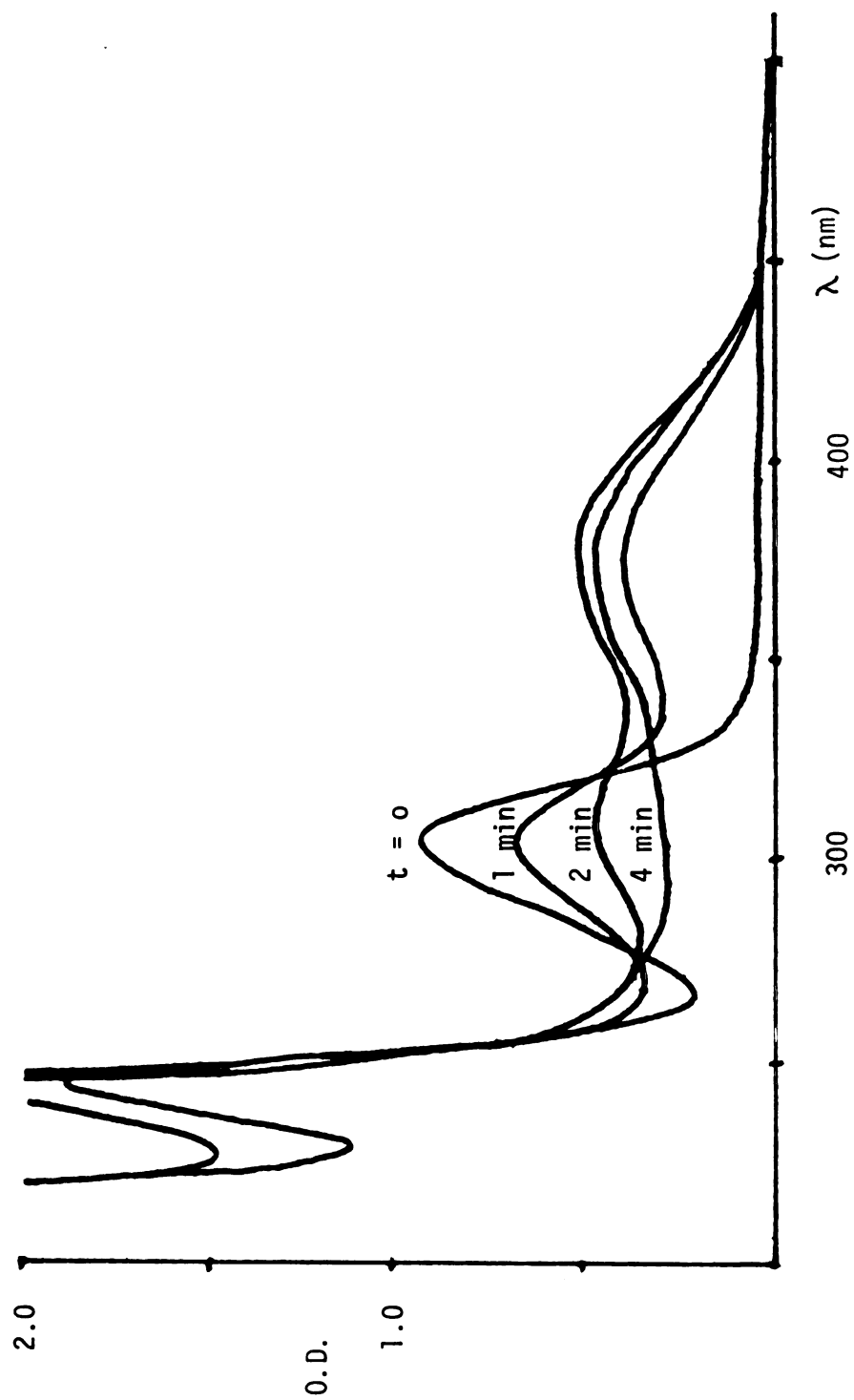


Figure 15. UV-Visible spectra of Q-AP₂₂ as a function of time of 313 nm irradiation in acetonitrile (2.45×10^{-4} M).

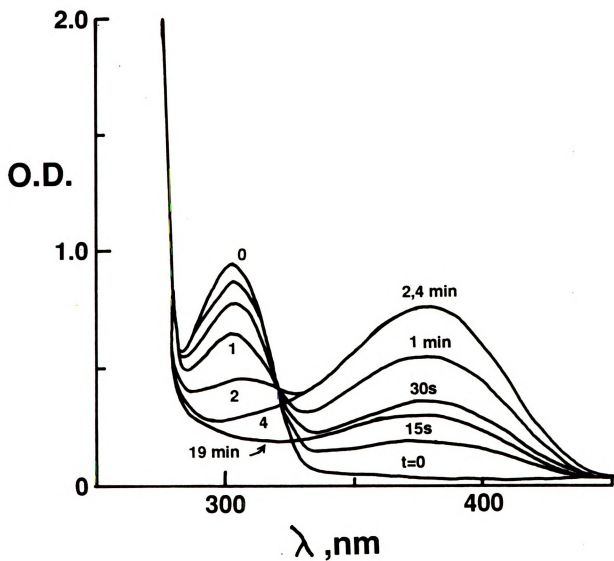


Figure 16. UV-Visible spectra of *o*-AP₂₂ as a function of time of 313 nm irradiation in benzene (2.45 × 10⁻⁴ M).

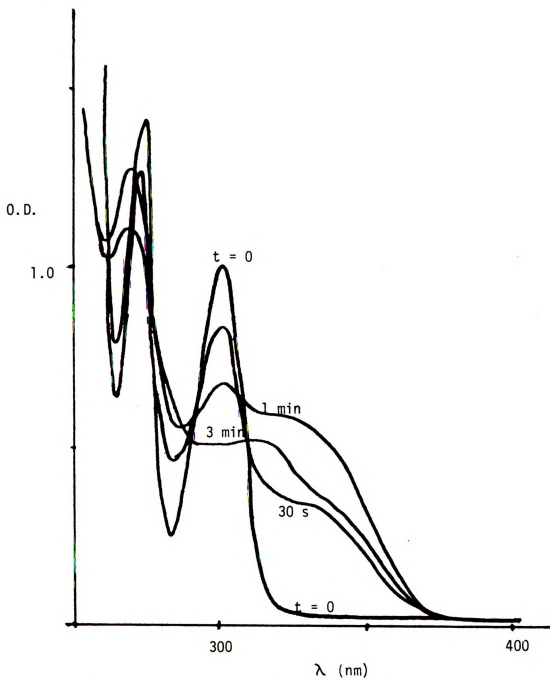


Figure 17. UV-Visible spectra of Ω -AP₂cis as a function of time of 313 nm irradiation in acetonitrile (1.4×10^{-4} M).

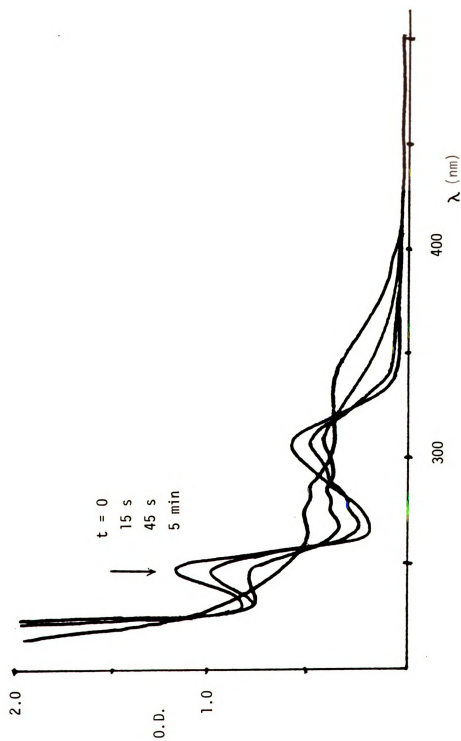


Figure 18. UV-Visible spectra of Q-AP₂₃ as a function of time of 313 nm irradiation in acetonitrile (1.61×10^{-4} M).

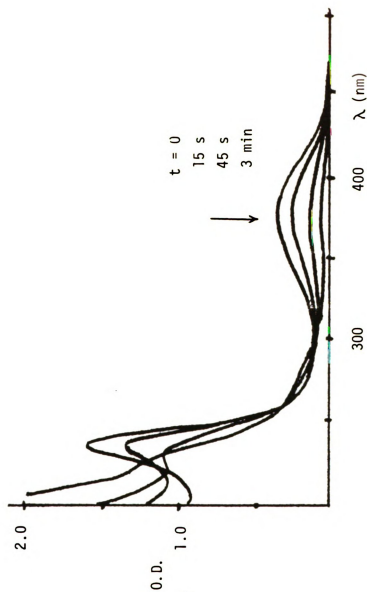


Figure 19. UV-Visible spectra of the cyclooctatriene from Q-AP₂₂ as a function of time of 313 nm irradiation in acetone.

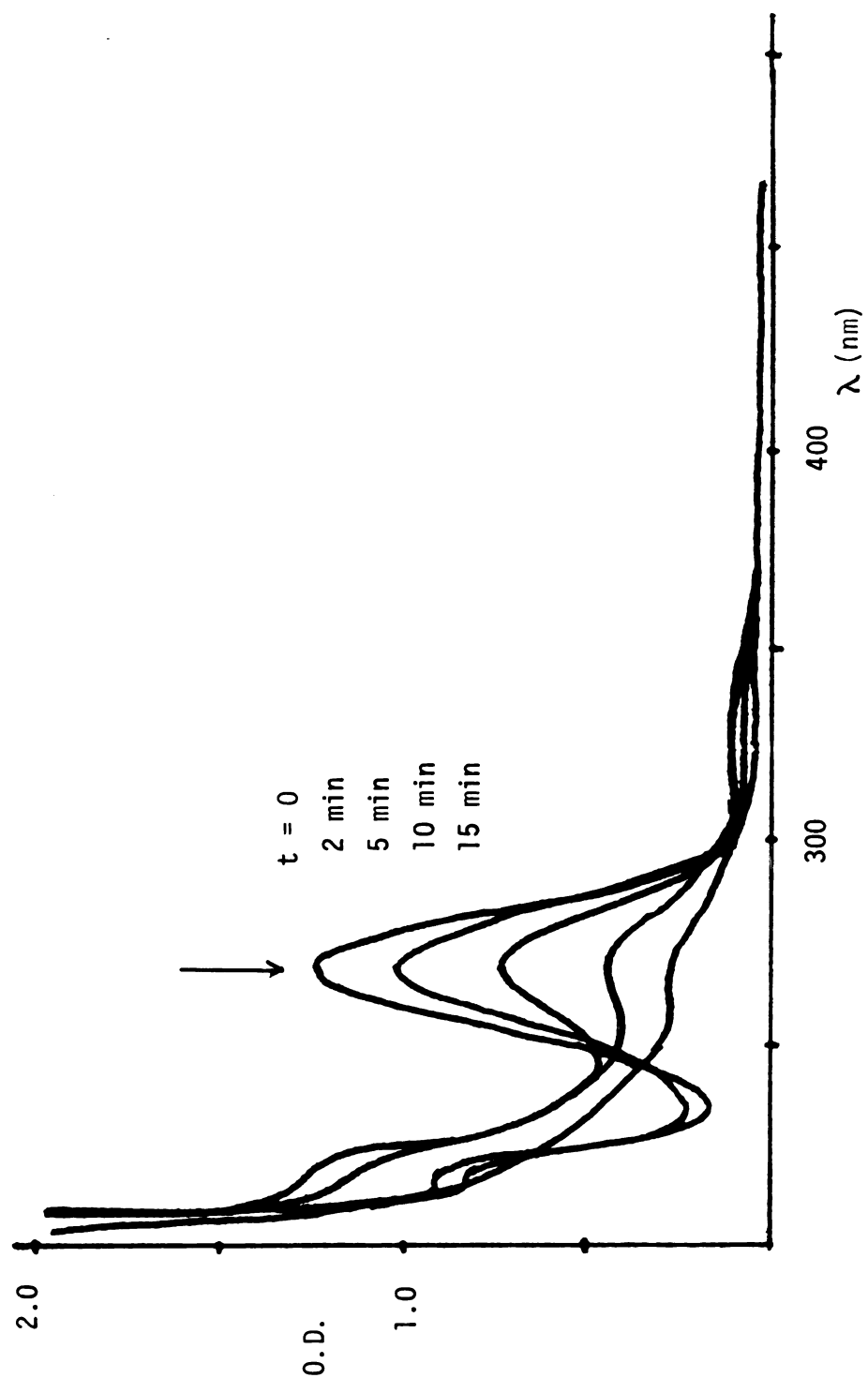


Figure 20. UV-Visible spectra of p-AP₂₁ as a function of time of 313 nm irradiation in acetonitrile (6.8×10^{-5} M).

tricyclic product. This ketone also showed new absorption around 320-370 nm upon irradiation, although it was weak (see Fig. 20).

3. Quantum Yields and Kinetic Results

a. Triplet Lifetime - About 0.01 M solution of a ketone with various amount of a quencher was degassed by the freeze-and-thaw method. The sample solutions were irradiated at 313 nm with the valerolphenone actinometer in a merry-go-round apparatus at room temperature.

The triplet lifetimes of the *p*-alkenoxyphenyl ketones changed dramatically with the chain length between the olefinic moieties and the phenyl groups. Among them, two methylene unit ketones, *p*-AP₂n and *p*-VP₂n, showed the shortest triplet lifetimes. Three methylene ketones, *p*-AP₃n and *p*-VP₃n, also presented some changes in the lifetime. The details are summarized in Table 8.

Photoisomerization of *cis*-*p*-VP₂2 to *trans*-*p*-VP₂2 was monitored by the Stern-Volmer plot within 15 % conversion. The $k_q\tau$ value for this process is 58 M⁻¹.

The values for $k_q\tau$ of *p*-VP₁1, *p*-VP₁2, and *p*-VP₁3 (all 0.01 M in acetonitrile) are 3700, 3270, and 1390 M⁻¹, respectively. These changes were assumed to be caused by the bimolecular self-quenching of the olefinic moieties of the ketones. To measure this bimolecular quenching, quantum yields

were determined by varying the concentration of a ketone. In other words, the ketone itself was considered as a quencher.

$$\Phi = \frac{P k_H \tau}{1 + k_{bi} \tau [K]}$$

$$1/\Phi = 1/\Phi_0 + (k_{bi}/(P k_H)) [K]$$

where P = probability to the triplet state

k_H = rate constant for hydrogen abstraction

k_{bi} = rate constant for quenching by a ketone

[K] = concentration of a ketone

Φ_0 = quantum yield extrapolated to [K] = 0

Plots of $1/\Phi$ vs. [K] gave straight lines with intercepts of $1/\Phi_0$ and slopes of $k_{bi}/(k_H P)$. As expected, the order for the values of the slopes and intercepts were $p\text{-VP}_13 > p\text{-VP}_12 > p\text{-VP}_11$ (Table 11).

For the ortho-alkenoxyphenyl ketones, $o\text{-VP}_2n$, two Stern-Volmer plots were made; one from the type II products and another from the cycloadducts. The photoproduct quantum yields and quenching results are given in Table 9.

The meta-alkenoxyvalerophenones were also measured by the Stern-Volmer plot. $m\text{-VP}_21$ and $m\text{-VP}_23$ have $k_q \tau$ values of 320, 90 M^{-1} (Table 10).

b. Quantum Yields - Quantum yields for the type II product formation and the cycloadduct formation was measured with the valerophenone actinometer ($\Phi = 0.33$).⁷⁵ The quantum

yields were calculated from the following equation and are given in Table 8,9 and 10:

$$\Phi = \frac{[\text{photoproduct}]}{[\text{acetophenone}]} \times 0.33$$

The solvent effect on the quantum yield for the formation of 1-acetyl-3-methyl-6-oxatricyclo[7.2.0]undec-7,10-diene from *o*-VP₂ was studied. The details are listed in Table 13.

4. Spectroscopy

a. Ultraviolet-Visible Spectra : UV-Visible absorption spectra in heptane were recorded for *o*- and *p*-alkenoxyphenyl ketones studied in this thesis. Each absorption maxima and molar extinction coefficients were listed on Table 14.

Also the absorption spectra of the photoproducts were measured when pure compounds were available. Those were written in the experimental part.

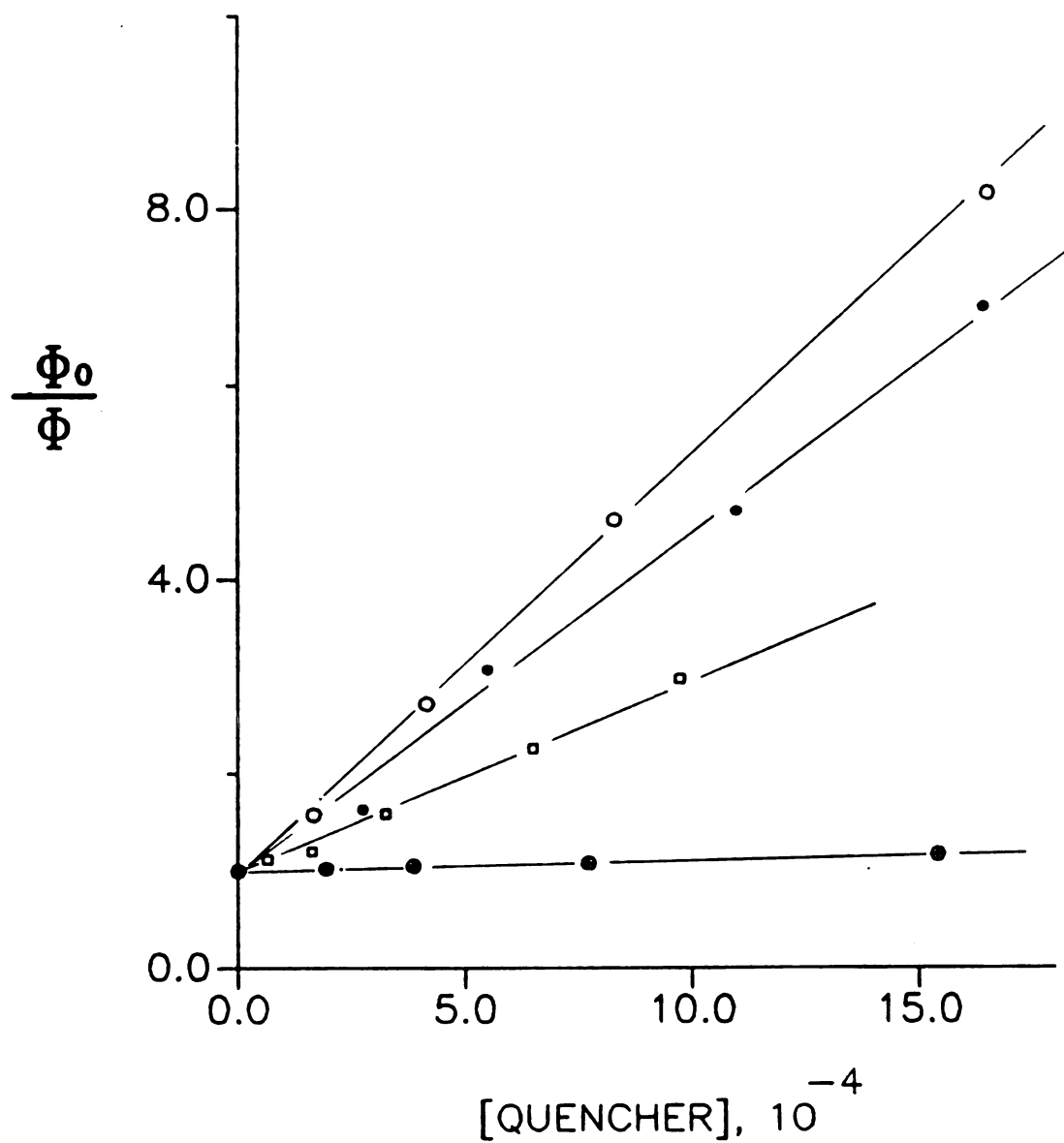


Figure 21. Stern-Volmer plots for the type II product formation of various p -VP_n1 in acetonitrile; VP₁1 (●), VP₂1 (⊕), VP₃1 (◻), VP₄1 (○).

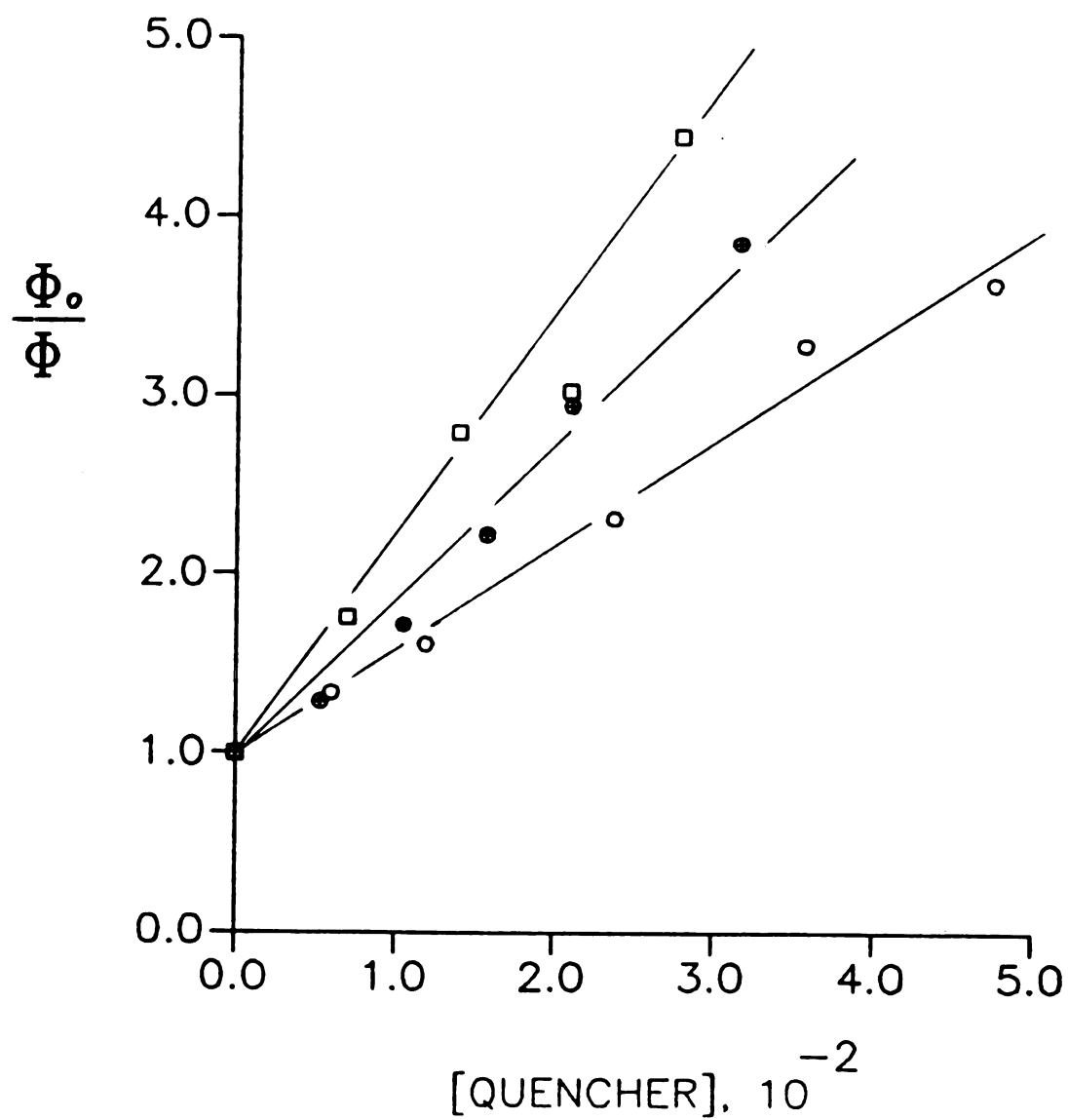


Figure 22. Stern-Volmer plots for the cycloadduct formation of various p -VP₂n in acetonitrile; VP₂1 ($\square$), VP₂2 ($\bullet$); VP₂cis ($\circ$) from the photoisomerization.

Table 8. Results of Stern-Volmer quenching of various *p*-alkenoxyvalerophenone by 2,5-dimethyl-2,4-hexadiene in acetonitrile (0.01 M) at 25 °C.

R	$k_q \tau_{II}^a$	$k_q \tau_c^b$	Φ_{II}^a	Φ_c^b
OCH ₃	4100	-	.17	-
OCH ₂ CH=CH ₂	3700	-	.15	-
OCH ₂ C(CH ₃)=CH ₂	3270	-	.14	-
OCH ₂ CH=C(CH ₃) ₂	1390	-	.045	-
O(CH ₂) ₂ CH=CH ₂	109	116	.0032	.028
O(CH ₂) ₂ C(CH ₃)=CH ₂	82	94	.0024	.027
cis-O(CH ₂) ₂ CH=CHC ₂ H ₅	-	58 ^c	.0016	.27 ^c
O(CH ₂) ₂ CH=C(CH ₃) ₂	-	-	.00022	-
O(CH ₂) ₃ CH=CH ₂	2050	-	.062	-
O(CH ₂) ₃ CH=C(CH ₃) ₂	1100	-	.040	-
O(CH ₂) ₄ CH=CH ₂	4370	-	.16	-
O(CH ₂) ₉ CH=CH ₂	4400	-	.17	-

^a for the Type II product formation. ^b for the cycloadduct formation. ^c for the cis-trans isomerization.

Table 9. Results of Stern-Volmer quenching of various α -alkenoxyvalerophenone by 2,5-dimethyl-2,4-hexadiene in benzene (0.01 M) at 25 °C.

R	$k_q\tau_{II}^a$	$k_q\tau_c^b$	Φ_{II}^a	Φ_c^b
OCH ₃	350	-	.20	-
O(CH ₂) ₂ CH=CH ₂	123	196	.046	.062
O(CH ₂) ₂ C(CH ₃)=CH ₂	37	31	.014	.20
O(CH ₂) ₂ CH=C(CH ₃) ₂ ^c	-	30	-	.19

^a for the Type II product formation. ^b for the cycloadduct formation. ^c from the acetophenone derivative.

Table 10. Results of Stern-Volmer quenching of various m-alkenoxyvalerophenone by 2,5-dimethyl-2,4-hexadiene in benzene (0.01 M) at 25 °C.

R	$k_q\tau_{II}^a$	$k_q\tau_C^b$	Φ_{II}^a	Φ_C^b
OCH ₃	350	-	.013	-
O(CH ₂) ₂ CH=CH ₂	320	-	.0073	-
O(CH ₂) ₂ CH=C(CH ₃) ₂	120	60	.0038	.0056 ^c

^a for the Type II product formation. ^b for the unknown product, whose molecular weight assumed to be that of the starting ketone. ^c estimated from the GC peak areas.

TABLE 11. The plot of $1/\Phi$ vs. the concentration of the ketones in acetonitrile.

Ketones	Intercept ^a	Slope ^b	$k_{bi}, 10^7$	$k_{CT}, 10^6$
p-VP ₁ 1	5.3	54	2.2	-
p-VP ₁ 2	9.9	155	6.5	1.7
p-VP ₁ 3	15	710	29.8	4.0

^a Intercept = $1/\Phi_0$. ^b Slope = $k_{bi}/(k_H P)$.

Table 12. Rate constants for the quenching of the triplet
p-methoxyvalerophenone by various olefins at 25 °C.

Olefins	Solvent	$k_q \tau^a$	$k_q^b, 10^6$
2-Me-1-pentene	CH ₃ CN	2.15	5.4
2-Me-2-pentene	CH ₃ CN	5.36	13
PhO-CH ₂ CH=CH ₂	benzene	1.58	2.0
PhO-CH ₂ C(Me)=CH ₂	benzene	4.51	5.6

^a from the methoxyacetophenone formation (see Table 25),
 $1/\tau = 2.44 \times 10^6$ (CH₃CN), $1.25 \times 10^6 \text{ s}^{-1}$ (benzene).

^b in $\text{M}^{-1}\text{s}^{-1}$.

Table 13. Quantum yield of ortho-(3-methyl-3-buten-1-oxy) valerophenone with 313 nm irradiation in various solvents.

Solvent	Φ_{II}	Φ_C
benzene	0.022	0.20
acetonitrile	0.012	0.20
methanol	<0.001 ^b	0.21
hexane	0.025	0.18
p-dioxane	0.053	0.17

^a from the valerophenone actinometer.

^b estimated from the GC peak.

Table 14. Ultraviolet-Visible absorption maxima^a for a series of alkenoxyphenyl ketones in heptane.

Ketone	L_a	$\pi \rightarrow \pi^*$	313-nm
α -VP0	241.4 (7910)	297.0 (3180)	1200
α -VP ₂ 1	241.8 (7560)	298.0 (3150)	1380
α -VP ₂ 2	240.8 (7700)	297.8 (3280)	1570
cis- α -VP ₂ 2	241.4 (7540)	298.0 (3070)	1320
α -AP ₂ 3	241.8 (9320)	299.6 (4120)	2420
5-Me- α -VP ₂ 2,	244.0 (8170)	308.9 (3620)	3380
4-Me-5-Cl- α -VP ₂ 2	246.2 (8240)	310.0 (4240)	4110
p -VP0	214.4 (14300)	263.4 (17900)	153
p -VP ₁ 1	214.4 (13300)	263.8 (18200)	109
p -VP ₂ 1	214.4 (13600)	264.6 (18700)	94
p -VP ₃ 1	214.4 (13400)	264.8 (18500)	58
p -VP ₄ 1	214.4 (13700)	265.0 (19000)	106

^a Values in parentheses are molar extinction coefficients.

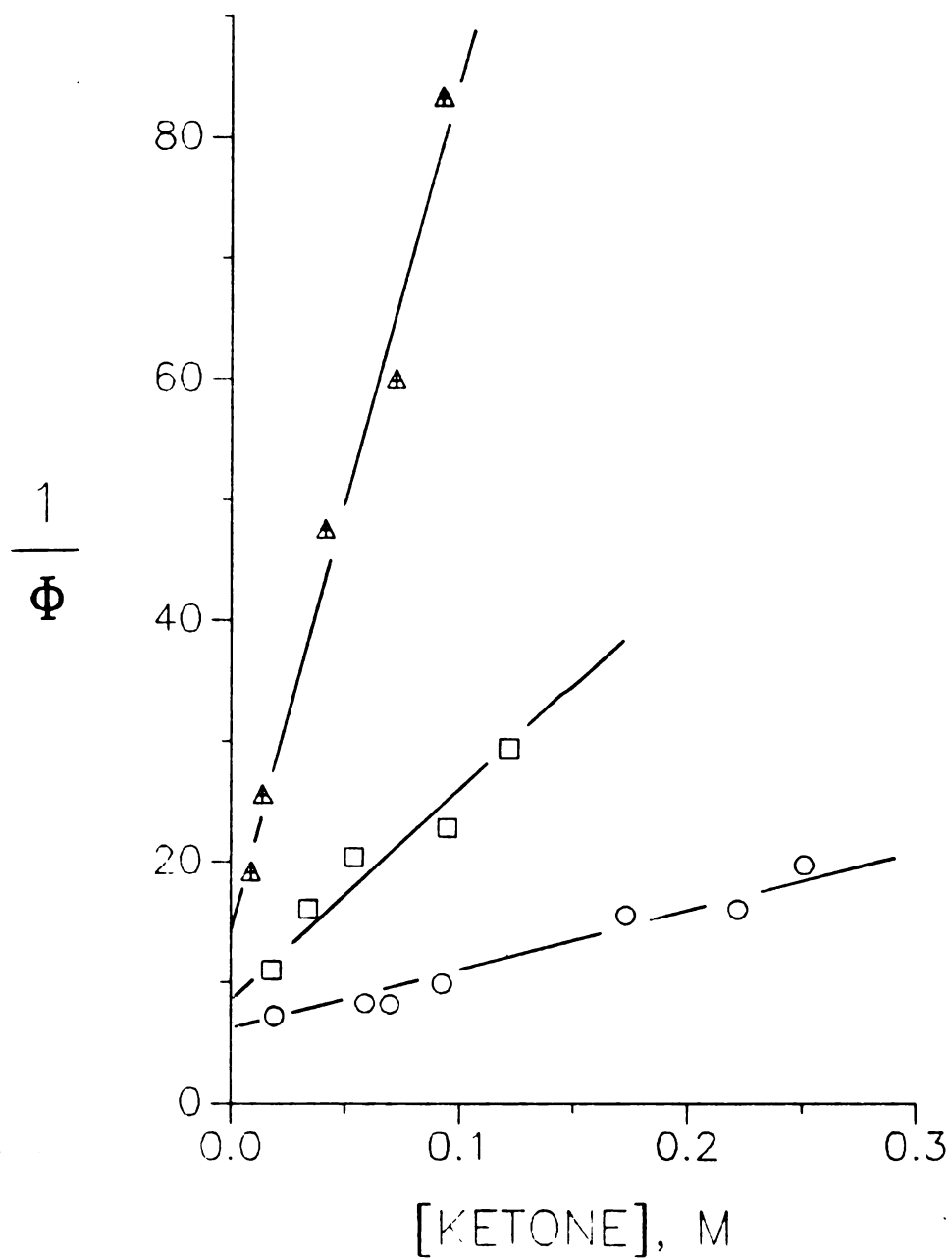


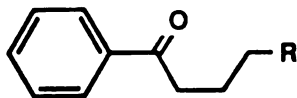
Figure 23. The dependence of the type II product formation of $p\text{-VP}_{1n}$ on the concentration of the ketones; $\text{VP}_1 1$ (○), $\text{VP}_1 2$ (◻), $\text{VP}_1 3$ (▲).

B. γ -Vinylbutyrophenones

Vinylbutyrophenones were synthesized from benzonitrile and the Grignard reagents of the corresponding vinyl alkyl bromide in THF.

Kinetic studies were performed in benzene solutions with 313 nm. The Stern-Volmer plots were obtained from the acetophenone formation. The ^1H -NMR spectra of some of the vinylbutyrophenones, which were irradiated in benzene- d_6 at 313 nm, showed at least two other products. One of them was assumed to be a cyclized product;⁷⁸ i.e., a 1-phenyl-3-cyclohexen-1-ol, and no further identification was performed.

The followings are the ketones studied in this thesis.



$\text{R} = \text{CH}=\text{CH}_2$	; BP1
$\text{cis-CH}=\text{CHEt}$	; BP2
$\text{CH}=\text{C}(\text{CH}_3)_2$	; BP3
$\text{cis-CH}_2\text{CH}=\text{CHEt}$	; VP2

1. Kinetic Results

The triplet lifetime of a ketone was determined by the Stern-Volmer quenching technique. The quantum yield was measured with the valerophenone actinometer, where the concentration of valerophenone was nearly the same as that of a vinyl ketone. The kinetic data are listed in Table 15 and 16.

The maximum quantum yield for acetophenone formation were obtained by adding pyridine in the ketones solution. Usually, 0.4-0.6 M of pyridine solution provided the maximum yield for acetophenone formation. Fig 25 shows the quantum yield dependence on the concentration of pyridine.

TABLE 15 . Result of Stern-Volmer quenching of $\text{PhCO}(\text{CH}_2)_3\text{-R}$ by 2,5-dimethyl-2,4-hexadiene in benzene at 25 °C.

R	$k_q \tau$	Φ	Φ_{max}
CH_3	47	.33	1.0
$\text{CH}=\text{CH}_2$	10.2	.28	.56
$\text{CH}=\text{CHEt}$	7.1	.13	.56
$\text{CH}=\text{CMe}_2$	3.2	.13	.47
$\underline{\text{Z}}\text{-CH}_2\text{CH}=\text{CHEt}$	33.5	.23	1.0

TABLE 16 . Result of Stern-Volmer quenching of $\text{PhCO}(\text{CH}_2)_3\text{-R}$ by 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25 °C.

R	$k_q \tau$	Φ	$1/\tau, 10^8$
$\text{CH}=\text{CH}_2$	15	0.17	6.67
$\text{CH}=\text{CHEt}$	4.7	0.20	21.3
$\text{CH}=\text{CMe}_2$	5.1	0.26	19.6
$\underline{\text{Z}}\text{-CH}_2\text{CH}=\text{CHEt}$	53	0.45	1.89

Table 17. Ultraviolet-Visible absorption^a of a series of γ -vinylbutyrophenones in heptane.

Ketone	$\pi \rightarrow \pi^*$	B-band	$n \rightarrow \pi^*$	other
VP	238 (12000)	278 (820)	323 (46)	286 (640)
-CH=CH ₂	238 (12400)	278 (940)	323 (47)	286 (740)
-CH=CH ₂ Et	238 (4900)	279 (330)	322 (36)	
-CH=C(Me) ₂	238 (12200)	278 (900)	324 (48)	286 (720)
-CH ₂ CH=CH ₂ Et	238 (12600)	278 (970)	324 (48)	286 (780)

^a Values in parentheses are molar extinction coefficients.

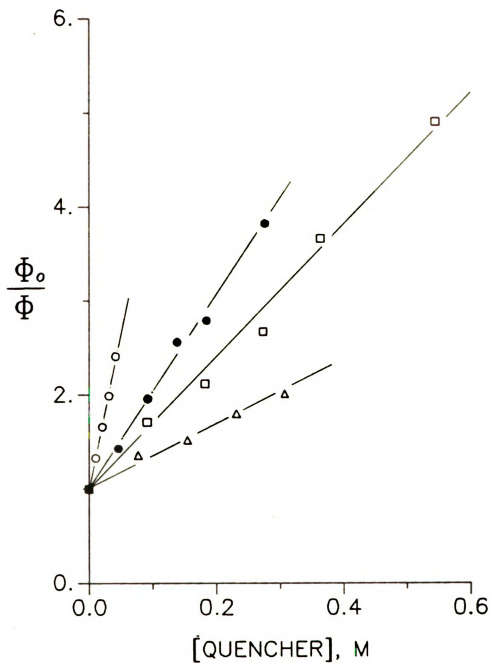


Figure 24. Stern-Volmer plots for acetophenone formation of various γ -vinylbutyrophenone in benzene; BP1 ($\bullet$), BP2 ($\square$), BP3 ($\triangle$), VP2 ($\circ$).

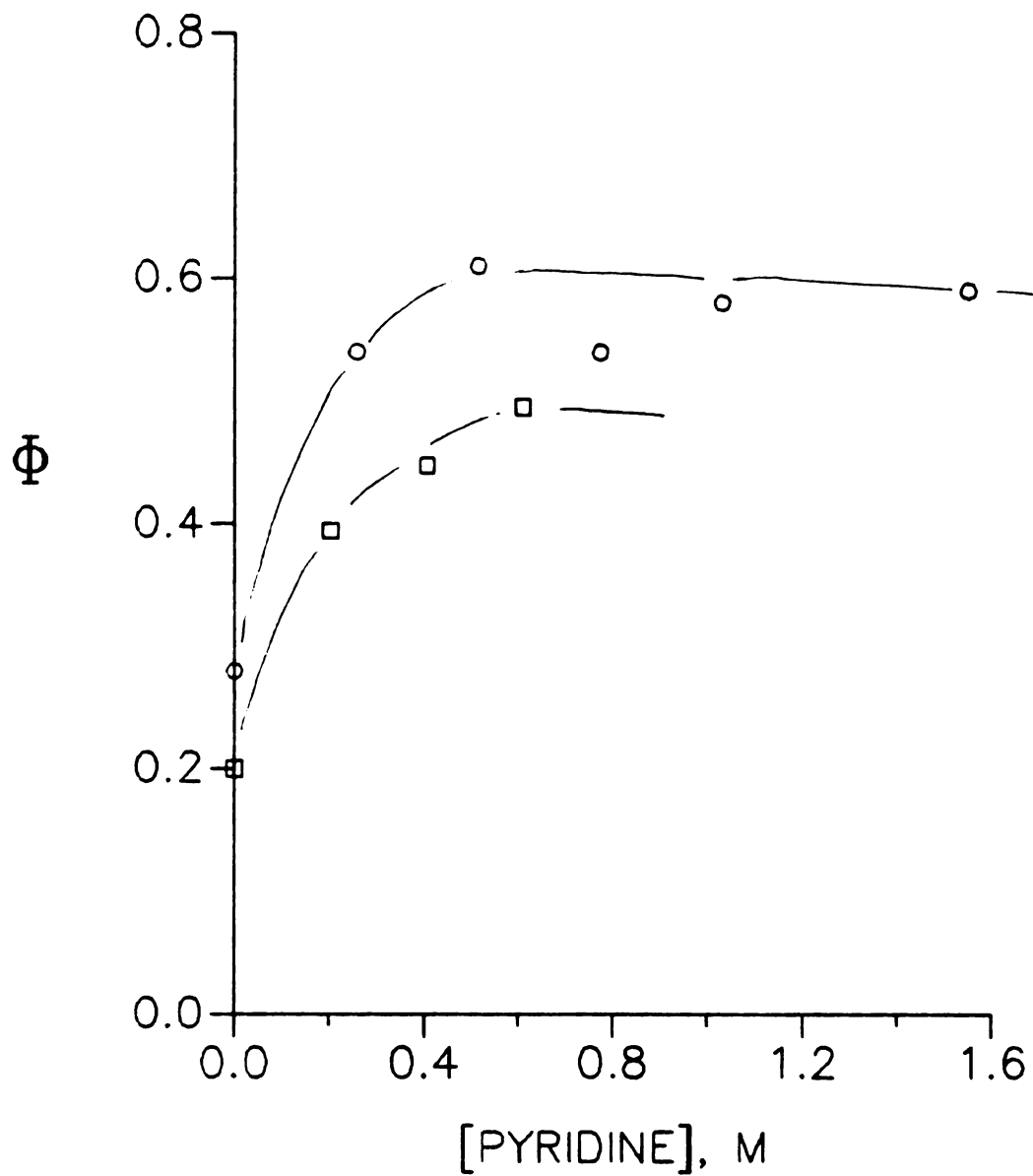


Figure 25. The effect of the pyridine concentration on the quantum yield for the acetophenone formation: from BP1 (O), from BP3 ($\square$).

DISCUSSION

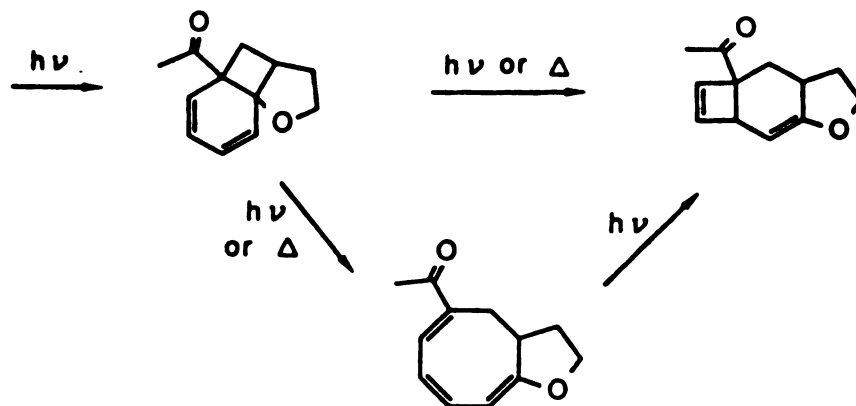
A. Alkenoxyphenyl Ketones

1. Cycloaddition

a. Cycloadducts - Photoproducts from ortho and para-alkenoxy phenyl ketones (o- or p-AP₂n) were identified as cyclobutene compounds. Now, the question is whether these cyclobutene products are 'direct' photoproducts or secondary photoproducts (two or more photons) or thermally driven from 'hot' photoproducts.

This question arose just because there are not many examples of such a photoreaction. The first possible mechanism for this reaction is that the intramolecular 1,2-addition of the olefinic moieties to the benzene rings photochemically, then the rearrangement to the cyclobutenes either thermally or photochemically. The second mechanism is that the 1,2-addition occurs first, then the adduct undergoes a ring opening to the cyclooctatriene either thermally or photochemically, finally this cyclooctatriene is converted to the tricyclo compound photochemically.

If the first mechanism is real, the conversion from the 1,2-adducts to the tricycloproducts will be very fast or the adducts will be very unstable, because time-based ¹H-NMR spectra of most ketones (except o-AP₂3) shows no peaks of the



cyclohexadiene even on short-time irradiation.

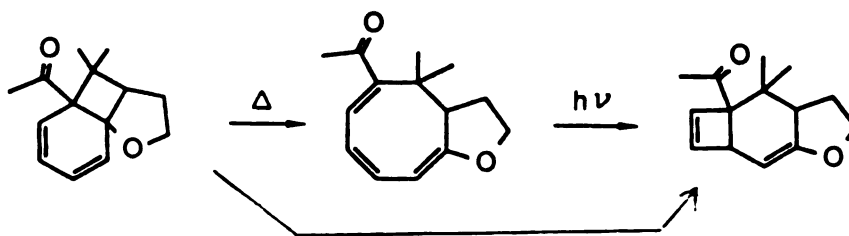
If this conversion is photochemical process, the cyclohexadiene will be sensitized to the tricyclo product by the starting ketone, because the extinction coefficient of the cyclohexadiene is not expected to be big enough for the direct irradiation.

Experimental data favor the second process. Especially, chronological UV-Visible absorption spectra of the alkenoxy phenyl ketones show a quick build-up of a new broad peaks at 340-390 nm. This would reflect the existence of a cyclooctatriene intermediate, because isolated cyclooctatrienes showed the absorption maxima at 340-370 nm. Thermal interconversion between bicyclo[4.2.0]octa-2,7-diene and cyclooctatriene is well known.⁸² Although the transient UV-visible absorption strongly supports the cyclooctatriene, we still do not know how fast the conversion from the cyclohexadiene to the cyclooctatriene is. But it can be assumed to happen in minutes, because even at lower concentration (ca. 10^{-4} M) of o-AP₂2 and

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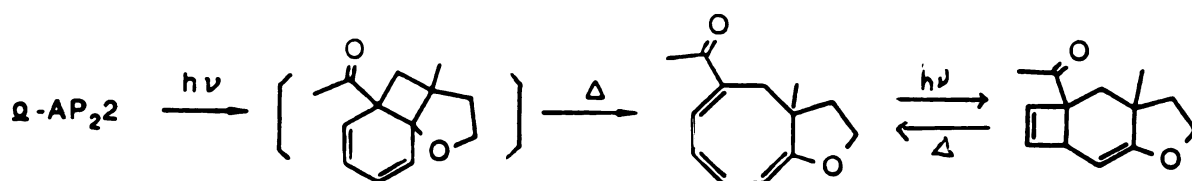
at low conversion, only a cyclooctatriene and a cyclobutene were observed by the ^1H -NMR (within 30 min) and UV-Visible spectra (within 5 min).

Another experimental data supporting the cyclooctatriene mechanism were obtained from the irradiation of *o*-AP₂3. The UV-Visible spectra of the ketone during irradiation showed weak new absorption at ca. 340 nm and another two absorption maxima at 285 and 270 nm. Irradiation of the same ketons (30-40 % conversion) yielded only one product whose ^1H -NMR shows the peaks of a cyclohexadiene. Two terminal methyl groups on the double bond could create steric hindrance in the cyclooctatriene structure and move the equilibrium toward the cyclohexadiene.^{82b,c} This valence tautomerism will be discussed in more details later. Eventually this intermediate was led to the cyclobutene product (Fig. 6). From this, we can get at least two important informations. The first one is that one of the 1,2-adducts (cyclohexadienes) was directly detected. The second one is that the cyclohexadiene is not converted to the cyclobutene via a photochemical way (direct irradiation or sensitization), because this ketone is the only one that yields the detectable cyclohexadiene even though every cyclohexadiene from other ortho ketones has the same chromophore (the same potential photoreaction, qualitatively and quantitatively).



However, there is important inconsistency in experimental data; in most cases, the time-based ^1H -NMR spectra do not show the cyclooctatriene peaks, but from UV-Visible spectra they were detected. For example, the time-based ^1H -NMR spectra of $\alpha\text{-AP}_22$ do not show any cyclooctatriene even at the very initial stage of the irradiation, but only the cyclobutene product appears (Fig 14). On the other hand, as seen in Fig 15 and 16 the absorption spectra of the same ketone show strong evidence for the formation of the cyclooctatriene intermediate.

But it has to be mentioned that for the ^1H -NMR spectra the concentration of the solution was usually 0.1-0.01 M, and for the UV-Visible spectra it was 10^{-4} - 10^{-5} M. At higher concentration of the starting ketones, it can be assumed that cyclooctatrienes undergo very efficient reaction to the tricyclic products, but at lower ketone concentration (100-1000 times lower) some amount of octatrienes were built up before the next transformation and detected on the UV-Visible absorption spectra. Actually, some amount of the octatriene



were observed with a tricyclic product on the ^1H -NMR spectrum upon the irradiation of a dilute solution (10^{-3} - 10^{-4} M).

Irradiation of 3-acethyl-1-methyl-9-oxabicyclo[6.3.0]undeca-3,5,7-triene collected by preparative GC (oven temperature 170°C) from the cyclobutene product of $\alpha\text{-AP}_22$, gave

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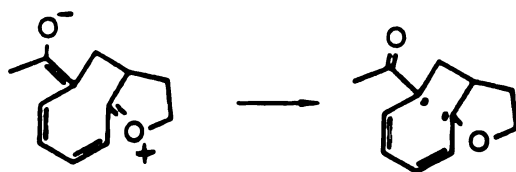
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the original tricyclo product, which means the cyclooctatriene and the tricyclo product interconvert photochemically from the former and thermally from the latter.

Here, the next question is how these cyclohexadienes were formed and converted to the cyclooctatrienes or the mechanism. There can be two answers for the question. The first one is a concerted 1,2-addition, the second one is a stepwise 1,2-addition. However, it is clear that the 1,2-addition is not synchronous process from the result that para-(cis-3-hexen-1-oxy)valerophenone undergoes very efficient isomerization ($\Phi = 0.27$). The rapid cyclohexadiene to cyclooctatriene rearrangement probably results from the weakened character of the middle C-C bond caused by donor-acceptor conjugation.

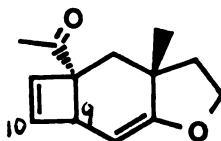


From the identification of the photoproducts of 2'-(3-methyl-3-buten-1-oxy)-5'-methoxyacetophenone and 2'-(3-methyl-3-buten-1-oxy)-4'-methyl-5'-chloroacetophenone, it is possible to determine the position of the aromatic carbons in the cyclobutene compounds. The former ketone showed two vinyl protons; a singlet at 5.49 ppm and a doublet at 4.99 ppm ($J = 6.7$ Hz). The singlet was assumed to be a cyclobutene vinyl

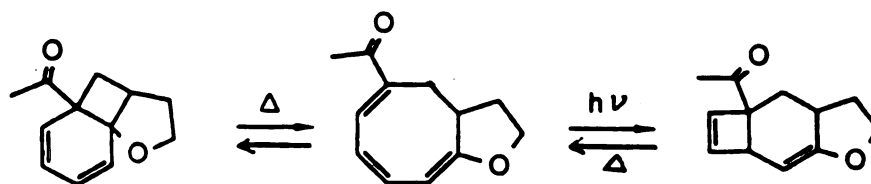
proton. Therefore, the methyl substituent has to be on the C-10. The chloro ketone gave one singlet at 6.72 ppm another singlet at 5.14 ppm on the ^1H -NMR spectrum. The chlorine atom is on the C-9. Therefore, the six carbons, C-1 and C-7 to C-11, come from the aromatic rings, and the sequence seems not to be changed.

Table 18 Selected chemical shift of tricycloproducts from α -(3-methyl-3-buten-1-oxy)acetophenone and its derivatives in C_6D_6 .

protons	<u>9,10 = H</u>		<u>9=H, 10=Me</u>		<u>9=Me, 10=Cl</u>	
	δ (ppm)	J(Hz)	δ	J	δ	J
H-11	5.78	2.8	5.49	-	6.72	-
H-10	5.86	2.8	-	-	-	-
H-9	3.26	6.6	3.16	6.7	-	-
H-8	4.96	6.6	4.99	6.7	5.14	-



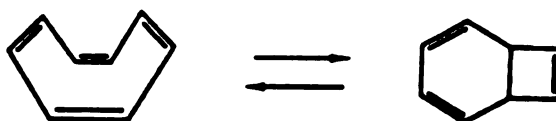
b. Thermal Rearrangement of Cycloadducts - In the cyclooctatriene system, there are two thermal rearrangement processes. The first one is the conversion between a bicyclo-[4.2.0]octa-2,4-diene (a cyclohexadiene) and a cycloocta-1,3,5-triene, and the second is that between a cyclooctatriene and a bicyclo[4.2.0]octa-2,7-diene which has a cis-fused cyclobutene.



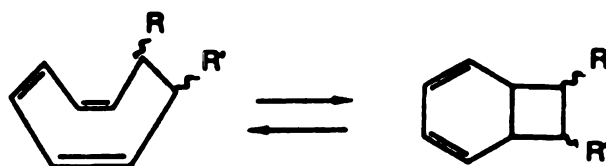
The second rearrangement is an irreversible one-way process thermally; only from a cyclobutene to a cyclooctatriene. The main products collected by a preparative GC (170-180 °C) are cyclooctatrienes by injecting the cis-fused cyclobutene products. This thermal rearrangement is symmetrically forbidden. But the rearrangement from the strained cyclobutenes to more stable all cis-cyclooctatrienes apparently happened. Again the middle C-C bond seems to be weakened by donor-acceptor conjugation between the carbonyl and the alkoxy group.

In the cyclooctatetraene tautomerism (3 π -bonds), the equilibrium concentration of the cis-fused cyclobutene was estimated to be 0.01 % at 100 °C, and its lifetime was calcu-

lated to be 14 min at 0 °C.⁸³ If our cyclobutenes had a trans-fused geometry (twisted 2 π -bonds), they could undergo symmetry-allowed rearrangement to the all-cis cyclooctatrienes even at low temperature, just like the allowed rearrangement of the above bicyclo[4.2.0]octatriene to cyclooctatetraene. But, the bicyclo[4.2.0]octa-2,7-dienes were stable in a refrigerator (ca. 0 °C) for weeks. Besides the NOE results, this is another indirect evidence for the cis-fused geometry of the cyclobutene photoproducts.



Valence tautomerism between bicyclo[4.2.0]octa-2,4-dienes and cycloocta-1,3,5-triene is known to be affected by the additional bulky groups on the ring.⁸³ When $R, R' = H$, the concentration of the bicyclic compound was 11 %, but when $R, R' = \text{methyl (trans)}$, it was 94 %. When $R = \text{two methoxys}$, the bicyclic population was measured to be >95 %.



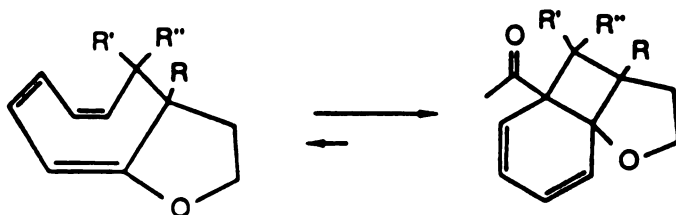
In our system with an extra 5-membered ring, R^1 is expected to have less steric hindrance because the extra ring

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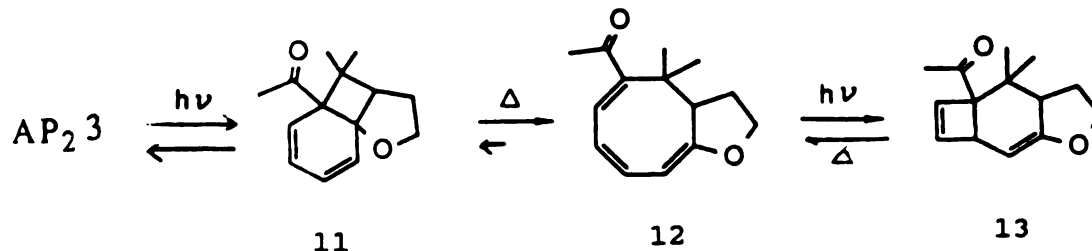
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twists the R^1 group outside of the cyclooctatriene. On the other hand, if R^2 is an bulky group, the steric hindrance can be estimated to be more severe than without the 5-membered ring. When $R^1, R^2, R^3 = H$, the energy-minimized conformation by the molecular mechanics calculation⁸⁴ has the dihedral angle of 35° between R^1 and R^2 . This is why irradiation of α -(4-methyl-3-penten-1-oxy)aceto-phenone affords a cyclohexadiene which is stable thermally. The methyl group at R^2 position dramatically reversed the equilibrium.



Rearrangement from 1-acetyl-2,2-dimethyl-6-oxabicyclo [7.2.0.0^{3,7}]undec-7,10-diene of α -AP₂3 to the cyclohexadiene reflects a change in the cyclohexadiene-cyclooctatriene interconversion. It can be concluded that some cyclooctatriene still is formed from 11, but the unfavorable equilibrium is offset by the irreversible photoisomerization of 12 to 13. Upon being heated, 13 opens to 12, which rearranges



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immediately to the thermodynamically preferred 11, which is unstable and interconverts with the starting ketone thermally.

The quantum yields for the cyclobutene formation should be higher than the values in Table 8 and 9, because the whole reaction is an two-photon process. From the equation of $\Phi_1\Phi_2 = \Phi_{\text{reported}}$, the range of each values will be $1 > \Phi_1 > \Phi_{\text{reported}}$ and $\Phi_{\text{reported}} < \Phi_2 < 1$, respectively.

2. Intramolecular Charge Transfer Quenching

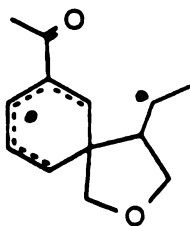
a. Charge Transfer Rate Constants - It is known that alkenes quench triplet ketones by a charge transfer process.⁸⁵ Quenching efficiency increases 3-4 times with each additional alkyl substituent on the double bond.

To figure out the charge transfer (CT) rate constants (k_{CT}), it is necessary to determine the rate constant for γ -hydrogen abstraction (k_{H}) and the intrinsic decay rate constant (k_{d}). Both k_{H} and k_{d} appear to be characteristics of chromophores. The k_{H} can be calculated from the equation $k_{\text{H}} = \Phi_{\text{II}}^{\text{max}}/\tau$ with the assumption that none of the biradicals reverts to the ground state ketone. The values for k_{H} in Table 19 were calculated from the values for Φ_{II} and represent the rate constants for the formation of the type II product rather than those for the formation of the biradical. However, the uniformity of the value for k_{H} for all the ketones studied presents the internal consistency of these data and this is not surprising because

all ketones have the same chromophore, an alkoxyphenyl alkyl ketone.

The exact process that determines the values of k_d for p-alkoxyphenyl ketones is not known. Typical values for k_d in phenyl ketones are on the order of 10^5 - 10^6 s⁻¹.⁸⁶ Wagner has found that the k_d values for p-methoxyphenyl alkyl ketones and the ortho derivatives are on the order of 1.6×10^6 and 1.1×10^7 s⁻¹, respectively.⁸⁷ It is unlikely that k_d values are sensitive to the nature of the alkoxy substituents, therefore, we can use the same values of k_d throughout the calculation.

The k_{CT} values in Table 19 equal to $1/\tau - k_H - k_d$. These k_{CT} values include both intramolecular and intermolecular quenching rate constants for the triplet p-alkenoxyphenyl ketones. In our system, $-O(CH_2)_nCH=CH_2$, intramolecular quenching appears only when $n = 2$ or 3. For the $n = 2$ phenyl ketone derivatives, intramolecular quenching rates are at least 100 times faster than the rates for the bimolecular quenching (Table 19). In the $n = 2$ ketones, the inner vinyl carbon can make a 5-membered ring with the two chain carbons, the oxygen, and the ipso carbon on the phenyl ring.



From the comparison of the k_{CT} values with the quantum yields for the photoproduct formation, it is clear that not all CT quenchings lead to the products. The rate constants for

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TABLE 19. Photokinetic data of *p*-alkenoxyvalerophenones in acetonitrile (0.01 M) at 25 °C.

KETONES	$1/\tau, 10^6$	Φ^a	$k_H, 10^5$	$k_d, 10^6$	$k_{CT}, 10^6$
<i>p</i> -VP ₀	2.44	.17	4.2	2.0	
<i>p</i> -VP ₁ 1	2.70	.15	4.1	2.0	0.3
<i>p</i> -VP ₁ 2	3.06	.14	4.3	2.0	0.7
<i>p</i> -VP ₁ 3	6.25	.045	2.8	2.0	4.0
<i>p</i> -VP ₂ 1	90.9	.0032	2.9	2.0	89
<i>p</i> -VP ₂ 2	122	.0037	4.5	2.0	120
<i>p</i> -VP ₂ cis		.0016			240 ^b
<i>p</i> -VP ₂ 3		.00022			1800 ^b
<i>p</i> -VP ₃ 1	4.88	.062	3.0	2.0	2.6
<i>p</i> -VP ₃ 3	9.0	.04	3.6	2.0	6.5
<i>p</i> -VP ₄ 1	2.3	.16	3.6	2.0	
<i>p</i> -VP ₉ 1	2.27	.17	3.9	2.0	

^a The Type II product formation. ^b estimated from the quantum yields.

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TABLE 20. Photokinetic data of *o*-alkenoxyvalerophenones in benzene (0.01 M) at 25 °C.

KETONES	$1/\tau, 10^7$	Φ_{II}^a	Φ_C^b	$k_H, 10^6$	$k_d, 10^7$	$k_{CT}, 10^7$
<i>o</i> -VP0	1.43	.18	-	2.6	1.2	-
<i>o</i> -VP ₂ 1	4.70	.046	.062	1.9	1.2	3.3
<i>o</i> -VP ₂ 2	14.7	.014	.20	2.1	1.2	13.3
<i>o</i> -AP ₂ 3 ^c	16.7	-	.19	-	1.2	15.5

^a for the Type II product. ^b for the cycloadduct

^c from acetophenone derivative.

Table 21. Photokinetic data of *m*-alkenoxyvalerophenone in benzene (0.01 M) at 25 °C.

Ketone	$1/\tau, 10^7$	Φ_{II}^a	$k_H, 10^5$	$k_d, 10^7$	$k_{CT}, 10^7$
<i>m</i> -VP0	2.86	.013	3.7	2.82	-
<i>m</i> -VP ₂ 1	3.13	.0073	2.3	2.82	0.3
<i>m</i> -VP ₂ 3	11.1	.0038	4.2	2.82	8.3

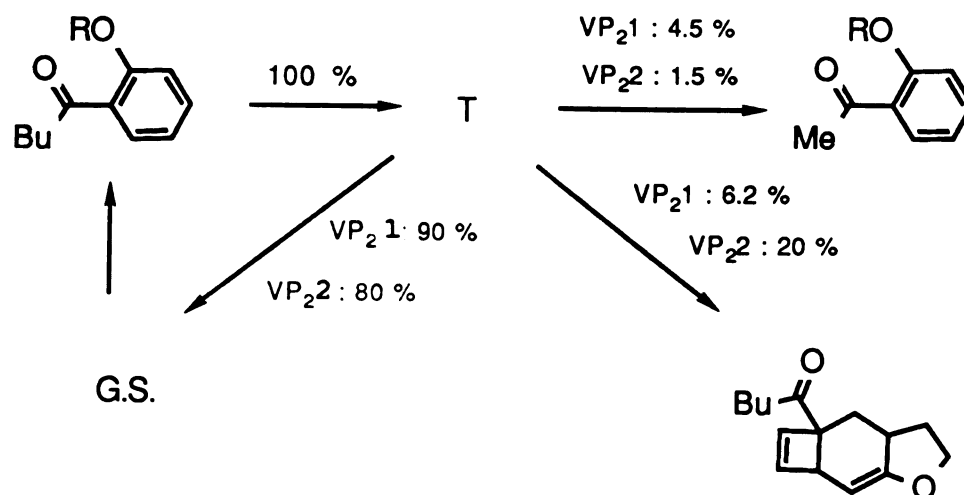
^a for the Type II product formation.

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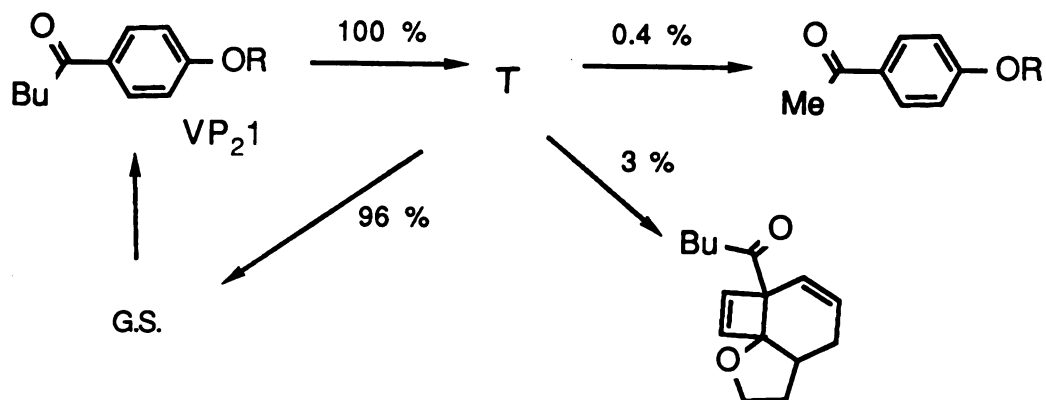
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the product formation, k_r , can be obtained from the expression $k_r = \Phi_r/\tau$. Therefore, the k_{CT} can be divided into the k_r and the unproductive k_q . The values for k_r represent the efficiency of the cycloaddition.

The meta derivatives also showed efficient intramolecular charge transfer quenching, but the adducts were not isolated so far. Unlike the ortho and para derivatives, the meta phenyl ketones solution did not give yellow color during irradiation. The unknown product detected from m-VP₂3 could be the cyclobutanol formed from the 1,4-biradical. Low or non-cycloadduct formation from the meta ketones upon irradiation, will be further research interests.

b. Regioselectivity - From the kinetic data, it is clear that in the intramolecular quenching there is tremendous regioselectivity favoring the structures which have two methylene units between phenoxy and olefins ($n = 2$), and its rate constants ($> 9 \times 10^7 \text{ M}^{-1}$) are bigger than those of the bimolecular processes (k_q of 1-hexene and 2-methyl-1-pentene; 5.4×10^6 and $1.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ in benzene, respectively).

The geometric requirement for the efficient quenching between chromophores and olefins seems to be more restricted than that of amines and alkylsulfides.²⁹ The chromophores of

o- and *p*-alkenoxypheⁿyl ketones are π, π^* lowest triplets, which locate their triplet energy around the phenyl rings. Therefore, the olefins can approach the excited benzene and act as electron donors.²⁸ The behavior of the phenyl ketones with $-O(CH_2)_2$ -vinyl might thus seem to fit best with the $n = 3$ rule for π -overlap shown by diarylalkanes.⁸⁸ More examples dealing with this entropic rule can be found in the α -phenyl- ω -alkenes system⁸⁹ and in the α, β -unsaturated ketones with alkene substituents.⁹⁰ The system with $-O(CH_2)_3$ -vinyl showed lower reactivity in the cycloaddition by at least 30 times.

Although the CT quenching efficiency of an olefin toward n, π^* triplets increases 3-4 times with each additional alkyl group on the double bond, the *p*-3-methyl-3-butenoxy derivatives (dialkyl olefins) show only a little more efficient quenching (1.5 times) than those of the butenoxy derivatives (monoalkyl olefins). This is similar to the addition of radicals to olefins; the cyclization of 5-hexenyl radical ($k = 10^5 \text{ s}^{-1}$) is little affected by alkyl substituents.⁹¹ In other words, the triplet benzene has both some radical and some positive charge characters. But we cannot exclude the possibility that this 'unexpected' result is caused by the intrinsically different quenching efficiency of the olefins to the π, π^* triplets from that to n, π^* triplets. The *p*-cis-3-hexenoxy and *p*-4-methyl-3-pentenox^y derivatives showed very low quantum yields for the type II product formation, which obviously indicates that the triplets decay faster and the quenched intermediates are better stabilized on secondary and tertiary carbons. If we assume the same $k_H = 4 \times 10^5 \text{ s}^{-1}$, the values

for k_{CT} of the dialkylated and the trialkylated olefins will be 2.4×10^8 and $1.8 \times 10^9 \text{ s}^{-1}$, respectively (Table 19). In radical chemistry, the rates for the addition of *t*-butoxy radical to olefins depend on the stability of the product radicals; i.e. the addition to isobutylene (tertiary radical) is 3.5 times more efficient than to 1-butene (secondary radical).⁹²

The fast isomerization ($\Phi = 0.26$) of *p*-cis-3-hexenoxy-phenyl ketones to their trans isomer, reveals that the cycloaddition mechanism is not a concerted process which is responsible for the cycloaddition of some singlet arenes to olefins.^{34a} The absorption of $S \rightarrow T$ transition of the ethylene occurs at 82 kcal/mole, which is accepted as the energy of a Frank-Condon transition to a planar ethylene triplet.⁹³ Triplet *p*-methoxyacetophenone ($E_T = 71.8 \text{ kcal/mol}$)²⁵ is, however, quenched by charge transfer process.^{85b} Therefore it is not likely that the isomerization is induced by the sensitization of triplet ketones.

From the facts discussed earlier, it can be assumed that there is a spiro-type intermediate in quenching and cycloaddition processes. This can be further supported by the steric effect of the olefins on the quantum yield for the cycloadduct formation. The cyclization rate of *o*-(4-methy-3-pentenoxo)acetophenone is not much faster than those of mono- or dialkylated olefinic ketones, even though it can make better stabilized tertiary radical intermediate and has better donor olefin moiety than mono- or dialkylated olefins. This retardation simply came from the steric hindrance between the

gem dimethyl groups on the double bond and the ortho acetyl group.

3. Triplets of Phenyl Ketones

a. π, π^* Phenyl Ketone Triplets - From the following experimental data, it is proved that the photocycloaddition occurred from the π, π^* triplets of the alkenoxyphenyl ketone systems; p-AP₂1 gave the cycloadduct in high chemical (> 95%) and quantum yield (0.03), but p-(3-buten-1-oxy)benzophenone for 48 hrs yielded an adduct (< 2 %) in very poor quantum yield. The main difference between the alkenoxyphenyl alkyl ketones and the alkenoxybenzophenones is that the former have the π, π^* lowest triplets and the latter have the n, π^* lowest triplets. The cycloadduct and the type II product of the former ketone are quenched well by 2,5-dimethyl-2,4-hexadiene, a known triplet quencher. Therefore, the efficient cycloaddition of alkenoxyphenyl alkyl ketones occurs from the lowest π, π^* triplets.

Another experimental evidence which supports this conclusion can be found from the dependence of the quantum yield on the solvents. The quantum yield for the type II product formation of o-(3-methyl-3-buten-1-oxy)valerophenone, o-VP₂2, was changed dramatically from 0.053 in p-dioxane to <0.001 in methanol. But those for the cycloadduct formation were not much affected by the change in solvents; 0.20 in benzene, 0.21 in methanol. In methanol, the type II quantum yield decreased

very much, and this is well fit by the fact that π, π^* triplet states are stabilized by polar solvents⁹⁴ and this reduced the equilibrium concentration of the upper n, π^* states. The consistency in the quantum yield for the cycloadduct formation gives another evidence for the cycloaddition from the π, π^* triplets.

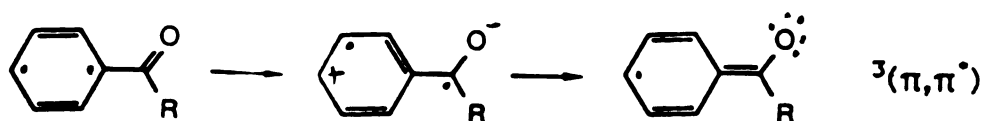
In photochemistry, it is not easy to figure out the electronic configuration of an excited state, simply because its lifetime is too short and its concentration is dilute enough to make difficulties in the analyses. However, if there is any chemical reaction from the excited states, many informations about them could be obtained from the photoproduct. As a matter of fact, this is one of the most general and safe way for that purpose.

The n, π^* triplets of phenyl ketones undergo well-known hydrogen abstraction, if the triplets are the lowest states and there are proper hydrogen donors. From the comparison of the properties of these triplets with those of alkoxy radicals, it is known that the n, π^* triplet has a biradical-type carbonyl group, i.e., one radical in the π^* orbital of the carbon and another in the half-filled n -orbital of the oxygen, therefore, it is very similar to alkoxy radicals.⁵

On the other hand, few photochemical reactions from the π, π^* triplets of phenyl ketones are known. The phenyl ketones substituted with electron-donating groups have the π, π^* lowest triplets and show dramatically reduced reactivity in the hydrogen abstraction. The hydrogen abstraction of alkoxyphenyl ketones having the lowest π, π^* triplets slows down as much as

200 times compared to that of an hydrogen-substituted phenyl ketone and explained to be caused by the equilibration between two different triplets.^{5,85b}

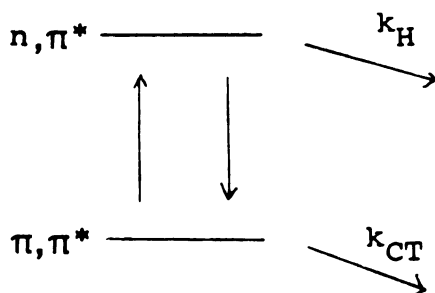
In the phenyl alkyl ketones, the carbonyl substituent stabilizes the π_a^* orbital and destabilizes the π_a orbital by mixing with the carbonyl π orbital, which enhances the contribution of the $\pi_a \rightarrow \pi_a^*$ transition to the $S \rightarrow L_a$ transition. The following valence bond representation describes the π, π^* triplets of phenyl ketones (3L_a).⁴



Although the 1,2-addition of an alkene to a triplet benzene was predicted to be allowed and concerted,^{34a} fast isomerization of cis-p-VP₂ to the trans ketone indicates that the cycloaddition of alkenoxyphenyl ketones is stepwise. The quenching efficiencies of the olefinic moieties toward the π, π^* triplets did not increase with additional alkyl substituent as much as expected from that toward the n, π^* triplets. The combined results once again suggest that the quinoidal forms of the π, π^* triplets are important resonance structures.

b. Equilibrium Between n, π^* and π, π^* Triplets - It is now well known that there is an equilibrium between n, π^* and π, π^* triplets of p-alkoxyphenyl ketones.^{19,85b} However, the

equilibrium constants between two triplets has never been studied. The two independent reactions from two equilibrated states make it possible to measure the equilibrium rate constants.⁹⁵ The cyclization reaction clearly occurs from the π, π^* triplet states of the ketones and hydrogen abstraction from the n, π^* triplet states. From this, it is possible to estimate the equilibrium rate constants:



As shown on Table 19 and 20, the values for the k_H of *p*- and *o*-alkenoxypheyl ketones were not changed significantly, while the k_{CT} values reached up to 10^8 . The consistency in k_H values means that the population of the upper n, π^* triplets does not change, i.e. still in an equilibrium state. It can be concluded that the value for k_1 , the rate constant for the conversion from the lowest π, π^* triplet to the upper n, π^* triplet, can be estimated to be bigger than k_c ($>10^8 \text{ s}^{-1}$). From the Boltzmann distribution law, the values for k_{-1} , the rate constant from the upper n, π^* triplet to the π, π^* triplet, can be also estimated to be $>10^{10} \text{ s}^{-1}$, because the equilibrium concentration of the n, π^* triplet is roughly 1/100 of the π, π^* triplet.

B. γ -Vinylbutyrophenones

1. Maximum Quantum Yield for the Type II Reaction

To determine the hydrogen abstraction rate, it is essential to measure the maximum quantum yield especially when the reactivity of γ -C-H's are different in a system. Wagner reported that hydrogen bonding by the Norrish Type II biradical to solvent molecules or a Lewis base suppresses reverse hydrogen abstraction of the biradical to the starting ketone and increases the yields for the type II product formation:⁹⁶



For valerophenone, the maximized quantum yield for acetophenone formation is unity with the addition of *t*-butyl alcohol.⁸¹ This indicates that the radiationless decay rate of the valerophenone triplet is slower than that of the type II cleavage. The 'absolute' hydrogen abstraction rate constant can be calculated from the expression $k_H = \Phi_{II}^{\max} / \tau$ and the intrinsic decay rate constant can be estimated to be less than 1/100 of the value for k_H ; i.e. for valerophenone, $k_H = 1.1 \times 10^8 \text{ s}^{-1}$ and $k_d \leq 10^6 \text{ s}^{-1}$. It is likely that this k_d value can be applied to the γ -vinylbutyrophenone system, because both have the same chromophore.

Fig. 25 shows the effects of pyridine on the quantum yield from 1-phenyl-5-hexen-1-one and 1-phenyl-6-methyl-5-hepten-1-one. Maximum quantum yield for the acetophenone formation can be obtained with ca. 0.6 M of pyridine.

2. Charge Transfer Quenching

As shown in Table 22, none of three vinylbutyrophenones has $\Phi_{\max} = 1$. Intramolecular CT transfer rate constants were calculated from the equation ($k_{CT} = 1/\tau - k_H - k_d$). Here, k_d was ignored as discussed earlier. Another thing has to be considered is the rate for the intersystem crossing, because alkenes are known to quench both singlet and triplet n, π^* ketones at comparable rates.^{85b,96} However, the rate for the intersystem crossing in phenyl ketones is close to 10^{10} - 10^{11} s⁻¹,² therefore no measurable singlet quenching would be expected in γ -vinylbutyrophenones.

There is a good correlation between hydrogen abstraction rate and C-H bond strength and inductive effect. Allylic hydrogen is 3-4 times more reactive toward hydrogen abstraction than the secondary alkyl hydrogen both by triplet benzoyl and by *t*-butyl radical.^{5,97} Each additional alkyl substituent on double bond increases the reactivity by 1.5 times.⁹² The hydrogen abstraction rate constant of 1-phenyl-5-hexen-1-one is about 2.5 times bigger than that of valerophenone and its CT quenching rate constant is 2.1×10^8 s⁻¹. This k_{CT} value is bigger than the value calculated originally³² and is well over its bimolecular version rate

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constant ($0.8 \times 10^7 \text{ s}^{-1}$). A half of triplet undergoes charge transfer quenching and another half leads to hydrogen abstraction. Each additional alkyl substituent on the double bond increases the k_H and also k_{CT} at the same time.

The calculated values for k_{CT} of various γ -vinylbutyrophenones do not show the trend that each additional alkyl group increases quenching efficiency by 3-4 times, but they increased by 1.5-2.5 times. Therefore, some fraction of k_{CT} seem to come from a radical reaction, which is similar to the intramolecular quenching process of the alkenoxyphenyl alkyl ketones. Actually the carbonyl of an n, π^* triplet is described as a kind of biradical, one electron on the carbon and another one on the oxygen.

A δ -vinylvalerophenone, 1-phenyl-cis-oct-6-en-1-one, does not show efficient quenching, but only γ -vinylbutyrophenones undergo efficient quenching process. From this, the quenching process between ketone chromophores and olefins requires a kind of 5-membered ring complex.

3. Products from γ -Vinylbutyrophenones

Besides the type II product, there were two more products observed from the GC analyses in all cases. However, the total

TABLE 22. Photokinetic data of $\text{PhCO}(\text{CH}_2)_3\text{-R}$ in benzene
(0.02 M) at 25 °C.

R	$k_q\tau$	Φ_{II}	Φ_{max}^a	$1/\tau, 10^8$	$k_H, 10^8$	$k_{CT}, 10^8$
CH_3	47	.33	1.0	1.06	1.06	-
CH=CH_2	10.2	.28	0.56	4.90	2.75	2.1
CH=CHEt	7.1	.13	0.56	7.04	3.94	3.1
CH=CMe_2	3.2	.13	0.47	15.6	7.33	8.1
$\text{Z-CH}_2\text{CH=CHEt}$	33.5	.23		1.49	-	-

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amount of those two was to be far less than 10 % of the product acetophenone, those were not identified, but just simply assumed as cyclic alcohols. γ -Hydrogen abstraction generates 1,4-biradicals, which convert to either acetophenone or cyclobutanols or 1,6-biradicals by simple resonance, which turn to cyclohexenols.⁸¹ But direct ^1H -NMR spectra after irradiation of BP1 and BP3 showed large amount of the same type of unknown products which could not be isolated so far. Analysis of these unknowns would be interesting and also give more informations of the whole processes.

C. Suggestion for Further Research

1. More about the Intermediates of 1,2-Cycloaddition

Undetected bicyclo[4.2.0]octa-2,4-dienes could be trapped by various dienophiles; for example, N-substituted triazolidenediones.



2. Synthetic Application of Photocycloaddition

Synthetic methods for the 8-membered rings have been always the challenge to organic chemists.⁹⁸ Certainly, the

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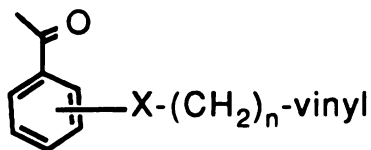
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high quantum and chemical yields for the cyclooctatriene formation from the alkenoxyphenyl ketones is a good news in that sense.

It would be useful to expand this reaction to other phenyl ketone systems. Instead of oxygen between arene and olefins, carbon, sulfur, and nitrogen could be used. The ester bond between them also would be tried.



X = carbon, sulfur, nitrogen, ester, etc.

Irradiation of p-methoxyacetophenone yielded 1,2-adduct with 1-hexene. Bimolecular cycloaddition of other substituted π, π^* triplet acetophenones to various olefins also would be a good trial for the synthetic purpose. This would give useful information of the electronic configuration of the π, π^* triplet phenyl ketones.

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EXPERIMENTAL

A. Preparation and Purification of Chemicals

1. Solvents and Additives

Benzene : One gallon of thiophene free reagent grade benzene was repeatedly stirred with 150 ml portions of sulfuric acid for 20-24 hr periods until the sulfuric acid remained colorless (about 5-6 times). The benzene and sulfuric acid were separated and the benzene washed with 500 ml portions distilled water twice, then with 200 ml of a saturated aqueous sodium bicarbonate solution until the aqueous phase remained neutral or basic. Then benzene was separated, dried over magnesium sulfate, and filtered into a 5 liter round bottom flask. To the flask phosphorus pentoxide was added and the solution was refluxed overnight. The benzene was distilled through a one meter column packed with stainless steel helices at a rate of 100 ml/hr. The first and last 10% were discarded.

Acetonitrile : Practical acetonitrile was first treated with benzoyl chloride according to the following procedure:⁹⁹
4 L of acetonitrile and 50 ml of benzoyl chloride were refluxed for 1 hr. Distill into a receiver containing 50 ml of water at 5-10 ml/min. Add 100 gr of Na_2CO_3 , reflux for 2 hr, then distilled into a receiver fitted with a drying tube. Add

50 gr of anhydrous Na_2CO_3 and 75 gr of KMnO_4 and distill at 5 to 10 ml/min with protection from atmospheric moisture. The distillate is made slightly acidic with concentrated sulfuric acid. Decant from precipitated ammonium sulfate and distill through 92 inch column packed with glass helices and repeat it again. The first and last 10% were discarded each times.

Methanol : Absolute methanol (1 L) was refluxed for 2 hr with magnesium turning (1 gr) and distilled. The first and last 10 % were discarded.

Pyridine : pyridine was refluxed over barium oxide overnight and distilled through a one meter column packed with glass helices. The first and last 10% were discarded.

2. Internal Standards

Pentadecane : Pentadecane (Columbia Organics) was washed with sulfuric acid and distilled (b.p. 131°C at 10 Torr.) by Dr. Peter J. Wagner.

Hexadecane : Hexadecane (Aldrich) was purified by washing with sulfuric acid, followed by distillation, b.p. 105°C (10 Torr) by Dr. Peter J. Wagner.

Heptadecane : Heptadecane (Chemical Samples Company) was purified by washing with sulfuric acid, then distilled by Dr. Peter J. Wagner. b.p. = 158 °C (8 Torr)

Methyl benzoate : Methyl benzoate (reagent grade) in ether was washed with aqueous sodium bicarbonate solution, with water, then dried over anhydrous sodium sulfate, finally distilled under reduced pressure.

n-Octyl benzoate : This was prepared by the reaction of benzoyl chloride with n-octyl alcohol. n-Octyl alcohol (40 gr) was added to benzoyl chloride (40 gr) in 200 ml ether. The solution was refluxed overnight with stirring. Then it was cooled, washed with water, extracted with ether, dried over anhydrous sodium sulfate, finally concentrated in vacuo. Distillation gave a clear liquid. ¹H-NMR spectrum confirmed the expected structure: b.p. 197-198 °C (0.5 torr); m/e 234 (M⁺).

3. Quenchers

2,5-Dimethyl-2,4-hexadiene : 2,5-Dimethyl-2,4-hexadiene (Chemical Samples Company) was allowed to sublime in the refrigerator.

Ethyl sorbate : It was used as received (Aldrich).

4. Ketones

4-Hydroxyvalerophenone and 2-hydroxyvalerophenone¹⁰⁰ :

Phenyl valerate was converted to the ketone by the Fries rearrangement.¹⁰¹ Aluminum chloride (270 gr, 2 moles) was placed in a three-necked flask equipped with a mechanical stirrer and heated to 70 °C on an oil bath. Phenyl valerate (80 gr, 0.5 mole, from phenol and valeryl chloride) preheated to 40 °C was added as quickly as possible. The reaction mixture was brought rapidly to 140 °C and stirred for 1 hour. Then the mixture was cooled to room temperature and hydrolyzed by adding 500 ml ice-cold 6 N hydrochloric acid. The solution was heated on a steam bath for half an hour and a viscous oil was separated. The aqueous layer was washed with 50 ml ether twice. The ether layer was combined with the oil and dried over magnesium sulfate. After evaporating ether under vacuo, the oil was vacuum-distilled to remove unreacted reactants and 2-hydroxyvalerophenone. The residual 4-hydroxyvalerophenone was recrystallized (pet ether-benzene): %Yield = 40 %; m.p. = 61-63 °C (Lit.¹⁰², 60-62 °C); ¹H-NMR (FT-80, CDCl₃) δ 0.93 (t, 3H), 1.15-1.85 (m, 4H), 2.92 (t, 2H), 6.80 (d, 2H), 7.75 (d, 2H).

2-Hydroxyvalerophenone was redistilled: %Yield = 35%; b.p. = 83-85 °C (0.1 torr); ¹H-NMR (60 MHz, CDCl₃) δ 12.2 (s, 1H, OH), 7.9-6.5 (m, 4H, Ar-H's), 2.9 (t, 2H, CH₂CO), 2.0-0.9 (m, 7H, CH₂CH₂CH₃); MS (m/e), 178 (M⁺), 149, 136, 121 (Base), 93, 65.

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4'-(2-Propen-1-oxy)valerophenone : 4-hydroxyvalerophenone (3.5 gr, 0.04 mole), allyl bromide (6 ml, 0.08 mole) and anhydrous potassium carbonate (5.6 gm, 0.04 mole) in 50 ml of dry acetone were refluxed for 40 hours under nitrogen atmosphere. After cooling down the solution, potassium bromide was filtered off. Acetone and the remained allyl bromide were evaporated under vacuo. The reaction mixture was dissolved in ether and washed with 20 ml of 2 N NaOH solution twice to remove unreacted 4-hydroxyvalerophenone, then washed with water and dried over magnesium sulfate. After the evaporation of ether the product was purified by the low temperature recrystallization in hexane to give colorless liquid: $^1\text{H-NMR}$ (FT-80, CDCl_3) δ 0.90 (t, 3H), 1.15-1.85 (m, 4H), 3.86 (t, 2H), 4.52 (d, 2H), 5.20-5.50 (m, 2H), 5.70-6.40 (m, 1H), 6.89 (d, 2H), 7.87 (d, 2H); MS (m/e) 218 (M^+), 176, 161 (base), 121, 105, 92, 77; IR (CCl_4) 2950, 2875, 1675 (C=O), 1600, 1225, 980 cm^{-1} ; UV (heptane), 214.4 (13300), 263.8 nm (18200).

4'-(2-Methyl-2-propen-1-oxy)valerophenone : This compound was synthesized from 4-hydroxyvalerophenone and 3-chloro-2-methylpropene (Aldrich) by the same method as that of p-(2-propenoxy) valerophenone. The product was recrystallized twice from hexane: m.p. = 29-30 $^{\circ}\text{C}$; $^1\text{H-NMR}$ (FT-80, CDCl_3) δ 0.92 (t, 3H), 1.2-1.9 (m, 4H), 1.80 (s, 3H), 2.86 (t, 2H), 4.9 (d, 2H), 6.87 (d, 2H), 7.87 (d, 2H); MS (m/e), 232 (M^+), 190, 175 (base), 161, 147, 121, 55; IR (CCl_4), 2940, 2875, 1675 (C=O), 1230, 1000 cm^{-1} .

1-Chloro-3-methyl-2-butene¹⁰³ : It was used just after being made. In a 100 ml round-bottomed flask were placed 17 ml (30 gr, 0.11 mole) of hexachloroacetone and 4.5 ml (3.7 gr, 0.05 mole) of 3-methyl-2-buten-1-ol (Aldrich). The solution was cooled to 0 °C and 13.5 gr (0.05 mole) of triphenylphosphine was added in small portions with stirring. After triphenylphosphine was dissolved completely (20 min), the brown solution was warmed up to room temperature. After 30 min the brown thick slurry was flash-distilled into a receiver in dry ice-acetone bath: ¹H-NMR (T-60, CDCl₃) δ 1.7 (d, 6H), 4.1 (d, 2H), 5.2-5.6 (m, 1H).

4'-(3-Methyl-2-buten-1-oxy)valerophenone : This ketone was made from 4-hydroxyvalerophenone and 1-chloro-3-methyl-2-butene by the same method as that of the propenoxy derivatives and recrystallized twice (hexane): m.p. = 41.5-42.5 °C; ¹H-NMR (250 Hz, CDCl₃), δ 0.93 (t, 3H), 1.38 (h, 2H), 1.67 (h, 2H), 1.74 (s, 3H), 1.78 (s, 3H), 2.89 (t, 2H), 4.55 (d, 2H), 5.47 (t, 1H), 6.91 (d, 2H), 7.91 (d, 2H); MS (m/e), 246 (M⁺), 232, 217, 204, 178, 136, 121 (base), 93, 69; IR (CCl₄), 2940, 1680 (C=O), 1600, 1225, 980 cm⁻¹.

4'-(3-Buten-1-oxy)valerophenone : This compound was synthesized from 1-bromo-3-butene (Aldrich) and 4-hydroxyvalerophenone: b.p. = 110-112 °C (0.1 Torr), ¹H-NMR (T-60, CDCl₃) δ 0.97 (t, 3H), 1.27-1.93 (m, 4H), 2.57 (m, 2H), 2.92 (t, 2H), 4.08 (t, 2H), 5.05-5.30 (m, 2H), 5.63-6.25 (m, 1H), 6.93 (d, 2H), 7.95 (d, 2H); ¹³C-NMR (CDCl₃) δ 198.9, 162.5,

133.8, 130.1, 130.0, 117.1, 114.0, 67.2, 37.6, 33.3, 26.5, 22.3, 13.8; MS (m/e), 232 (M^+), 190, 175, 121 (base), 55; IR (CCl_4), 2960, 2940, 2870, 1680 (C=O), 1600, 1245, 1170 cm^{-1} ; UV (heptane), 214.4 (13600), 264.6 (18700) nm.

4'-(4-Penten-1-oxy)valerophenone : This was made from 1-bromo-4-pentene (Aldrich) and p-hydroxyvalerophenone. b.p. = 119-121 °C (0.1 Torr). 1H -NMR ($FT-80$, $CDCl_3$) δ 0.90 (t, 3H), 1.20-2.00 (m, 6H), 2.20 (m 2H), 2.88 (t, 2H), 4.00 (t, 2H), 4.90-5.20 (m, 2H), 5.80-6.10 (m, 1H), 6.90 (d, 2H), 7.90 (d, 2H); ^{13}C -NMR ($CDCl_3$) δ 199.1, 162.8, 137.5, 130.2, 130.0, 115.3, 114.1, 67.3, 37.9, 29.9, 28.2, 26.7, 22.5, 13.9; MS (m/e), 246 (M^+), 217, 204, 189, 136, 121 (base), 104, 93; IR (CCl_4), 2925, 1675 (C=O), 1600, 1575, 1225 cm^{-1} ; UV (heptane), 214.4 (13400), 264.8 nm (18500).

4'-(5-Hexen-1-oxy)valerophenone : 5-Hexen-1-ol (Aldrich) was converted to the tosylate, which was then reacted with 4-hydroxyvalerophenone. 5-hexen-1-ol (5 gr, 0.05 mole) was dissolved in 25 ml pyridine. The solution was cooled in ice-water bath. p-Toluenesulfonyl chloride (11 gr, 0.057 mole) was added by portions. After 3 hr stirring at 0 °C, 10 ml of conc sulfuric acid with 50 gr of ice was added, then the solution was extracted with ether. The organic layer was washed with 2 N NaOH solution once, with water twice, then dried over sodium sulfate. After the evaporation of ether, a slightly yellowish oil was obtained, which was used in next step without further purification:

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$^1\text{H-NMR}$ (FT-80, CDCl_3) for the tosylate: δ 1.25-1.75 (m, 4H), 2.00 (m, 2H), 2.45 (s, 3H), 4.00 (t, 2H), 4.80-5.00 (m, 2H), 5.50-6.00 (m, 1H), 7.30 (d, 2H) 7.75 (d, 2H).

For the ketone: b.p. = 132-133 $^\circ\text{C}$ (0.1 Torr), $^1\text{H-NMR}$ (FT-80, CDCl_3), δ 0.90 (t, 3H), 1.15-1.90 (m, 6H), 2.10 (m, 2H), 2.88 (t, 2H), 4.00 (t, 2H), 4.90-5.10 (m, 2H), 5.55-6.05 (m, 1H), 6.90 (d, 2H), 7.90 (d, 2H); MS (m/e), 260 (M^+), 218, 203, 136, 121 (base), 104, 93, 55; IR (CCl_4), 2925, 1675 (C=O), 1600, 1250, 1170 cm^{-1} ; UV (heptane), 214.4 (13700), 265.0 nm (19000).

4'-(9-Undecen-1-oxy)valerophenone : 9-Undecen-1-ol

(Aldrich) was converted to the tosylate by the same method with 1-hexen-1-ol. The ketone was purified on column chromatography (silica gel, hexane): $^1\text{H-NMR}$ (CDCl_3), δ 7.85 (d, 2H), 6.84 (d, 2H), 5.82-5.65 (m, 1H, $-\text{CH}=\text{C}$), 4.98-4.82 (m, 2H, $\text{C}=\text{CH}_2$), 3.92 (t, 2H, $-\text{OCH}_2-$), 2.83 (t, 2H, $\text{CH}_2\text{C=O}$), 1.80-1.50 (m, 4H), 1.45-1.10 (m, 16H), 0.90 (t, 3H); IR (CCl_4), 2925, 2850, 1675 (C=O), 1600, 1360, 1250, 1175 cm^{-1} ; MS (m/e), 330 (M^+), 288, 275, 136, 121 (base), 91, 55.

1-Bromo-4-methylpent-3-ene¹⁰⁴ : 0.5 mole (42 gr) of cyclopropyl methyl ketone in 50 ml of ether was added slowly to the Grignard solution of methyl iodide (0.55 mole). The solution was heated up for 30 min, then hydrolyzed with saturated NH_4Cl solution. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether solution was washed with water twice, dried (MgSO_4), then

ether was evaporated to give 2-cyclopropylpropan-2-ol, which was used in the next step without further purification. 40 gr of the alcohol in 250 ml flask was cooled in ice-water bath. 47% HBr solution (160 ml) was added slowly over 10 min with stirring. The mixture was warmed to 40 °C and kept another 10 min, then extracted with ether. The ether layer was washed several time with water, once with saturated NaHCO₃ solution, again with water. The ether solution was dried (MgSO₄), evaporated. The halide (38 gr) was collected between 60-63 °C at 25 Torr. The overall yield was 50%.

¹H-NMR (FT-80, CDCl₃) : δ 1.65 (s, 3H), 1.72 (s, 3H), 2.55 (m, 2H), 3.40 (t, 2H), 5.10 (m, 1H).

4'-(4-Methyl-3-penten-1-oxy)valerophenone : This ketone was made from p-hydroxyvalerophenone and 1-bromo-4-methyl-3-pentene: m.p. = 36.5-37.5 °C, ¹H-NMR (FT-80, CDCl₃) δ 0.90 (t, 3H), 1.50 (m, 4H), 1.62 (s, 3H), 1.72 (s, 3H), 2.45 (m, 2H), 2.85 (t, 2H), 3.95 (t, 2H), 5.20 (m, 1H), 6.88 (d, 2H), 7.88 (d, 2H); ¹³C-NMR (CDCl₃) δ 199.1, 162.8, 134.7, 130.2, 130.0, 119.2, 114.1, 67.8, 37.9, 28.0, 26.7, 25.7, 22.5, 17.8, 13.9; MS (m/e) 260 (M⁺), 218, 136, 121, 83, 55 (base); IR (CCl₄), 2970, 2945, 2885 (aliphatic C-H's), 1680 (C=O), 1600 (C=C), 1250, 1170 cm⁻¹.

4'-(3-Methyl-3-buten-1-oxy)valerophenone : This ketone was made from p-hydroxyvalerophenone and the corresponding tosylate which was prepared by the usual way from 3-methyl-3-buten-1-ol: b.p. = 110-112 °C, ¹H-NMR (FT-80, CDCl₃) δ 0.95

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(t, 3H), 1.50 (m, 4H), 1.80 (s, 3H), 2.50 (t, 2H), 2.85 (t, 2H), 4.15 (t, 2H), 4.80 (s, 2H), 6.90 (d, 2H), 7.90 (d, 2H); ^{13}C -NMR (CDCl_3) δ 199.1, 162.2, 141.7, 130.2, 130.1, 114.1, 112.2, 66.6, 37.9, 37.0, 26.7, 22.7, 22.5, 13.9; MS (m/e), 246 (M^+), 204, 189, 136, 121 (base), 41; IR (CCl_4), 2970, 2940, 2880, 1680 (C=O), 1600, 1245, 1170 cm^{-1} .

4'-((Z)-3-Hexen-1-oxy)valerophenone : The ketone was synthesized from hydroxyvalerophenone and the bromide of (Z)-3-hexen-1-ol (Alfa). The alcohol was converted to the tosylate, which was reacted with potassium bromide to make (Z)-1-bromo-3-hexene as described before. The ketone was recrystallized (hexane) at low temperature and is a colorless liquid at room temperature: ^1H -NMR (250 MHz, CDCl_3) δ 0.95 (t, 3H), 1.00 (t, 3H), 1.50 (m, 4H), 2.11 (m, 2H), 2.56 (m, 2H), 2.85 (t, 2H), 4.00 (t, 2H), 5.45 (m, 2H, CH=CH , $J = 10.7$ Hz), 6.90 (d, 2H), 7.90 (d, 2H); ^{13}C -NMR (CDCl_3) δ 199.1, 162.7, 134.6, 130.2, 130.1, 123.6, 114.1, 67.7, 37.9, 27.1, 26.7, 22.5, 20.6, 14.2, 13.9; MS (m/e), 260 (M^+), 218, 203, 136, 121, 83, 55 (base); I.R. (CCl_4), 3030 (aromatic C-H), 2970, 2950, 2885 (aliphatic C-H's), 1685 (C=O), 1600 (C=C), 1250, 1160 cm^{-1} .

1-Bromo-5-methyl-4-hexene and (Z)-1-bromo-4-heptene : These bromides were made from the one carbon-shorter bromides.¹⁰⁵ In a 500 ml round bottomed flask, were placed 25 gr of magnesium (0.19 mole) and 25 ml of THF. Magnesium was

activated with 0.5 ml of 1,2-dibromoethane and 0.5 ml of 1-bromo-4-methyl-3-pentene. Then 30 gr of the bromide (0.19 mole) in 100 ml THF was added slowly to keep gentle reflux over 30 min. After another 15 min on a steam bath, 6 gr of paraformaldehyde (0.2 mole, dried in vacuum overnight with phosphorous pentoxide) was added, then the solution was stirred overnight at room temperature. 100 ml of saturated ammonium chloride solution was added and the aqueous layer was extracted with ether. The ether solution was washed with saturated sodium chloride solution and dried over sodium sulfate, then ether was evaporated. Finally 5-methyl-4-hexen-1-ol (15.5 gr, 71 %) was fractionated at 92-95 °C (30 Torr): $^1\text{H-NMR}$ (FT-80, CDCl_3) δ 1.61 and 1.69 (2s, 2 CH_3 's), 3.36 (t, 2H), 5.13 (m, 1H).

The alcohol was converted to the tosylate and finally to 1-bromo-5-methyl-4-hexene: bp₇₀ = 92-95 °C; $^1\text{H-NMR}$ (FT-80, CDCl_3) δ 1.64, 1.70 (2s, 2 CH_3 's), 3.40 (t, 2H), 5.08 (m, 1H); I.R. (CCl_4), 3025 (aromatic C-H), 2975, 2895 (aliphatic C-H's), 1680 (C=O), 1600 (C=C), 1250, 1170 cm^{-1} .

4'-((Z)-4-hepten-1-oxy)valerophenone : This was made from (Z)-1-bromo-4-heptene and p-hydroxyvalerophenone: b.p. = 156-158 °C (0.1 Torr). $^1\text{H-NMR}$ (CDCl_3), δ 7.93 (d, 2H), 6.92 (d, 2H), 5.50-5.30 (m, 2H, $\text{CH}=\text{CH}$, $J = 10.9$ Hz), 4.03 (t, 2H), 2.89 (t, 2H), 2.22 (m, 2H), 2.03 (m, 2H), 1.85 (m, 2H), 1.70 (m, 2H), 1.40 (m, 2H), 0.95 (t, 3H), 0.93 (t, 3H): $^{13}\text{C-NMR}$ (CDCl_3) δ 119.1, 162.9, 132.9, 130.2, 130.0, 127.5, 114.1, 67.3, 37.9, 28.9, 26.7, 23.3, 22.5, 20.4, 14.2, 13.9; MS (m/e), 274, 232,

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217, 136, 121 (base), 55; I.R. (CCl_4), 3025, 2975 2895, 1680 (C=O), 1600 (C=C), 1250, 1170 cm^{-1} .

4'-(3-buten-1-oxy)benzophenone : This ketone was obtained from 4-hydroxybenzophenone (Aldrich) and 1-bromo-3-butene (Aldrich) by the same method as that for the acetophenone derivatives; $^1\text{H-NMR}$ (CDCl_3) δ 7.80 (m, 4H), 7.50 (m, 3H), 6.97 (d, 2H), 5.85-6.00 (m, 1H), 5.25-5.15 (m, 2H), 4.12 (t, 2H), 2.58 (m, 2H); MS (m/e), 252 (M^+), 198, 121 (base), 105, 77, 55; IR (CCl_4), 3050, 2925, 2875, 1665 (C=O), 1600, 1250 cm^{-1} .

Ortho-alkenoxyphenyl ketones : The following method was used for all ketones. 0.7 gr of metal sodium was added to ethyl alcohol flushed by nitrogen bubbling. After sodium was dissolved, equimolar amount of o-hydroxyphenyl ketone was added to the solution. After 30 min stirring at room temperature, slight excess of a corresponding alkenyl bromide was added, then refluxed overnight under nitrogen atmosphere. The solvent was changed to ether, and the solution was washed with aqueous KOH solution three times, then ether was evaporated. The product ketones were usually purified by vacuum distillation.

2'-(3-Buten-1-oxy)acetophenone : This is a liquid and was recrystallized at low temperature in hexane: $^1\text{H-NMR}$ (250 MHz, C_6D_6) δ 8.02 (d, 1H), 7.07 (m, 1H), 6.75 (m, 1H), 6.40 (d, 1H), 5.67-5.50 (m, 1H), 4.88-5.00 (m, 2H), 3.42 (t, 2H), 2.52

(s, 3H), 2.09 (m, 2H); MS (70 eV, m/e), 190 (M^+), 1175, 162, 149, 136, 121, 91, 77, 55 (base); IR (CCl_4), 3075, 2930, 1675 (C=O), 1600, 1450, 1290, 1240, 1050 cm^{-1} .

2'-(3-Buten-1-oxy)valerophenone : This was recrystallized in hexane: m.p. 25-28 °C, 1H -NMR (250 MHz, $CDCl_3$), δ 7.64 (d, 1H), 7.40 (m, 1H), 6.97 (m, 1H), 6.85 (m, 1H), 6.00-5.80 (m, 1H), 5.20-5.10 (m, 2H), 4.10 (t, 2H), 2.93 (t, 2H), 2.55 (m, 2H), 1.70-1.55 (m, 2H), 1.45-1.30 (m, 2H), 0.95 (t, 3H); MS (70 eV, m/e), 232 (M^+), 203, 190, 175, 162, 147, 133, 121 (base), 105, 93, 77, 65, 55; IR (CCl_4), 2960, 1675 (C=O), 1600, 1450, 1250, 1050 cm^{-1} ; UV (heptane), 209.6 (24200), 241.8 (7560), 298.0 nm (3150).

2'-(3-Methyl-3-buten-1-oxy)acetophenone : This was vacuum-distilled: b.p. 98-100 °C (0.1 Torr); 1H -NMR (250 MHz, C_6D_6) δ 8.02 (d, 1H), 7.06 (m, 1H), 6.74 (m, 1H), 6.42 (d, 1H), 4.73 (br.s, 1H), 4.65 (br.s, 1H), 3.57 (t, 2H), 2.53 (s, 3H), 2.10 (t, 2H), 1.51 (s, 3H); MS (70 eV, m/e), 204 (M^+), 189, 159, 149, 136, 121 (base), 91, 69; IR (CCl_4), 2925, 1680 (C=O), 1600, 1450, 1290, 1230, 890 cm^{-1} .

2'-(3-Methyl-3-buten-1-oxy)valerophenone : This was vacuum-distilled: b.p. 129-130 °C (0.1 Torr); 1H -NMR (250 MHz, $CDCl_3$) δ 7.62 (d, 1H), 7.49 (m, 1H), 6.95 (m, 1H), 6.91 (d, 1H), 4.84 (br.s, 1H), 4.80 (br.s, 1H), 4.15 (t, 2H), 2.97 (t, 2H), 2.54 (t, 2H), 1.78 (s, 3H), 1.62 (qn, 2H), 1.43 (h, 2H), 0.90 (t, 3H); MS (70 eV, m/e), 246 (M^+), 231, 217, 204, 189,

147, 136, 121 (base), 69; IR (CCl_4), 2960, 1675 (C=O), 1600, 1450, 1290 cm^{-1} ; UV (heptane), 209.6 (24700), 240.8 (7700), 297.8 nm (3080).

2'-(cis-3-Hexen-1-oxy)acetophenone : This was distilled: b.p. 114-115 $^{\circ}\text{C}$ (0.1 Torr); $^1\text{H-NMR}$ (250 Mz, CDCl_3) δ 7.74 (d, 1H), 7.43 (m, 1H), 6.97 (m, 1H), 6.93 (d, 1H), 5.40-5.63 (m, 1H), 4.08 (t, 2H), 2.62 (s, 3H), 2.59 (m, 2H), 2.10 (m, 2H), 0.98 (t, 3H); MS (70 eV, m/e), 218 (M^+), 149, 136, 121, 882, 67, 55 (base); IR (CCl_4), 2960, 1650 (C=O), 1600, 1450, 1025 cm^{-1} .

2'-(cis-3-Hexen-1-oxy)valerophenone : This was distilled: b.p. 142-144 $^{\circ}\text{C}$ (Torr); $^1\text{H-NMR}$ (250 MHz, C_6D_6) δ 7.92 (d, 1H), 7.07 (m, 1H), 6.77 (m, 1H), 6.46 (d, 1H), 5.50-5.25 (m, 1H), 3.51 (t, 2H), 3.01 (t, 2H), 2.24 (m, 2H), 1.91 (m, 2H), 1.82 (m, 2H), 1.35 (m, 2H), 0.89 (t, 3H), 0.87 (t, 3H); MS (70 eV, m/e), 260 (M^+), 178, 149, 136, 121, 105, 82, 67, 55 (base); IR (CCl_4), 2960, 2930, 1645 (C=O), 1600, 1450, 1230, 1025 cm^{-1} ; UV (heptane), 209.6 (25400), 241.4 (7540), 298.0 nm (3070).

2'-(4-Methyl-3-Penten-1-oxy)acetophenone : This was distilled at 111-113 $^{\circ}\text{C}$ (0.1 Torr): $^1\text{H-NMR}$ (250 MHz, C_6D_6) δ 8.03 (d, 1H), 7.06 (m, 1H), 6.75 (m, 1H), 6.45 (d, 1H), 5.06 (m, 1H), 3.48 (t, 2H), 2.54 (s, 3H), 2.18 (m, 2H), 1.59 (s, 3H), 1.43 (s, 3H); MS (70 eV, m/e), 218 (M^+), 149, 136, 121, 82, 67, 55 (base); IR (CCl_4), 2975, 2930, 1675 (C=O), 1600,

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(s, 3H), 2.09 (m, 2H); MS (70 eV, m/e), 190 (M^+), 1175, 162, 149, 136, 121, 91, 77, 55 (base); IR (CCl_4), 3075, 2930, 1675 (C=O), 1600, 1450, 1290, 1240, 1050 cm^{-1} .

2'-(3-Buten-1-oxy)valerophenone : This was recrystallized in hexane: m.p. 25-28 °C, 1H -NMR (250 MHz, $CDCl_3$), δ 7.64 (d, 1H), 7.40 (m, 1H), 6.97 (m, 1H), 6.85 (m, 1H), 6.00-5.80 (m, 1H), 5.20-5.10 (m, 2H), 4.10 (t, 2H), 2.93 (t, 2H), 2.55 (m, 2H), 1.70-1.55 (m, 2H), 1.45-1.30 (m, 2H), 0.95 (t, 3H); MS (70 eV, m/e), 232 (M^+), 203, 190, 175, 162, 147, 133, 121 (base), 105, 93, 77, 65, 55; IR (CCl_4), 2960, 1675 (C=O), 1600, 1450, 1250, 1050 cm^{-1} ; UV (heptane), 209.6 (24200), 241.8 (7560), 298.0 nm (3150).

2'-(3-Methyl-3-buten-1-oxy)acetophenone : This was vacuum-distilled: b.p. 98-100 °C (0.1 Torr); 1H -NMR (250 MHz, C_6D_6) δ 8.02 (d, 1H), 7.06 (m, 1H), 6.74 (m, 1H), 6.42 (d, 1H), 4.73 (br.s, 1H), 4.65 (br.s, 1H), 3.57 (t, 2H), 2.53 (s, 3H), 2.10 (t, 2H), 1.51 (s, 3H); MS (70 eV, m/e), 204 (M^+), 189, 159, 149, 136, 121 (base), 91, 69; IR (CCl_4), 2925, 1680 (C=O), 1600, 1450, 1290, 1230, 890 cm^{-1} .

2'-(3-Methyl-3-buten-1-oxy)valerophenone : This was vacuum-distilled: b.p. 129-130 °C (0.1 Torr); 1H -NMR (250 MHz, $CDCl_3$) δ 7.62 (d, 1H), 7.49 (m, 1H), 6.95 (m, 1H), 6.91 (d, 1H), 4.84 (br.s, 1H), 4.80 (br.s, 1H), 4.15 (t, 2H), 2.97 (t, 2H), 2.54 (t, 2H), 1.78 (s, 3H), 1.62 (qn, 2H), 1.43 (h, 2H), 0.90 (t, 3H); MS (70 eV, m/e), 246 (M^+), 231, 217, 204, 189,

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147, 136, 121 (base), 69; IR (CCl_4), 2960, 1675 ($\text{C}=\text{O}$), 1600, 1450, 1290 cm^{-1} ; UV (heptane), 209.6 (24700), 240.8 (7700), 297.8 nm (3080).

2'-(cis-3-Hexen-1-oxy)acetophenone : This was distilled: b.p. 114-115 $^{\circ}\text{C}$ (0.1 Torr); ^1H -NMR (250 Mz, CDCl_3) δ 7.74 (d, 1H), 7.43 (m, 1H), 6.97 (m, 1H), 6.93 (d, 1H), 5.40-5.63 (m, 1H), 4.08 (t, 2H), 2.62 (s, 3H), 2.59 (m, 2H), 2.10 (m, 2H), 0.98 (t, 3H); MS (70 eV, m/e), 218 (M^+), 149, 136, 121, 882, 67, 55 (base); IR (CCl_4), 2960, 1650 ($\text{C}=\text{O}$), 1600, 1450, 1025 cm^{-1} .

2'-(cis-3-Hexen-1-oxy)valerophenone : This was distilled: b.p. 142-144 $^{\circ}\text{C}$ (Torr); ^1H -NMR (250 MHz, C_6D_6) δ 7.92 (d, 1H), 7.07 (m, 1H), 6.77 (m, 1H), 6.46 (d, 1H), 5.50-5.25 (m, 1H), 3.51 (t, 2H), 3.01 (t, 2H), 2.24 (m, 2H), 1.91 (m, 2H), 1.82 (m, 2H), 1.35 (m, 2H), 0.89 (t, 3H), 0.87 (t, 3H); MS (70 eV, m/e), 260 (M^+), 178, 149, 136, 121, 105, 82, 67, 55 (base); IR (CCl_4), 2960, 2930, 1645 ($\text{C}=\text{O}$), 1600, 1450, 1230, 1025 cm^{-1} ; UV (heptane), 209.6 (25400), 241.4 (7540), 298.0 nm (3070).

2'-(4-Methyl-3-Penten-1-oxy)acetophenone : This was distilled at 111-113 $^{\circ}\text{C}$ (0.1 Torr): ^1H -NMR (250 MHz, C_6D_6) δ 8.03 (d, 1H), 7.06 (m, 1H), 6.75 (m, 1H), 6.45 (d, 1H), 5.06 (m, 1H), 3.48 (t, 2H), 2.54 (s, 3H), 2.18 (m, 2H), 1.59 (s, 3H), 1.43 (s, 3H); MS (70 eV, m/e), 218 (M^+), 149, 136, 121, 82, 67, 55 (base); IR (CCl_4), 2975, 2930, 1675 ($\text{C}=\text{O}$), 1600,

1450, 1190, 1230 cm^{-1} ; UV (heptane), 209.6 (31400), 241.8 (9320), 299.6 nm (4120).

2'-(3-methyl-3-buten-1-oxy)-5'-methylacetophenone : This ketone was prepared from 1-bromo-3-methyl-3-butene and 2-acetyl-4-methylphenol which was made from 4-methylphenyl acetate by the Fries rearrangement: $^1\text{H-NMR}$ (CDCl_3), δ 7.50 (d, 1H, $J = 2.8$ Hz), 7.24 (d of d, 1H, $J = 2.8, 8.5$ Hz), 6.83 (d, 1H, $J = 8.5$ Hz), 4.82 (br. s, 2H), 4.10 (t, 2H), 2.65 (s, 3H), 2.60 (m, 2H), 2.28 (s, 3H), 1.80 (s, 3H); MS (70 eV), m/e 218 (M^+), 203, 173, 163, 150, 135 (base), 121, 69; IR (CCl_4), 2925, 1675 (C=O), 1240, 900 cm^{-1} ; UV (heptane), 213.2 (27500), 244.0 (8170), 308.8 nm (3620).

2'-(3-methyl-3-butenoxy)-5'-chloro-4-methylacetophenone : This ketone was prepared from 1-bromo-3-methyl-3-butene and 2-acetyl-4-chloro-5-methylphenol which was made from 3-methyl-4-chlorophenyl acetate by the Fries rearrangement: $^1\text{H-NMR}$ (CDCl_3), δ 7.69 (s, 1H), 6.76 (s, 1H), 4.82 (br. s, 2H), 4.15 (t, 2H), 2.56 (s, 3H), 2.54 (m, 2H), 2.37 (s, 3H), 1.80 (s, 3H); MS (70 eV), m/e 254:252 (1:3, M^+), 186:184 (1:3), 171:169 (1:3), 77, 69 (base); IR (CCl_4), 2930, 1680 (C=O), 1600, 1375, 1255, 1225 cm^{-1} ; UV (heptane), 217.8 (32500), 246.2 (8240), 310.0 nm (4240).

m-Hydroxyvalerophenone : 1-Bromobutane (41 gr, 0.3 mole) was turned to the Grignard solution with magnesium turning (7.5 gr, 0.32 mole) in THF. m-Methoxybenzonitrile (32 gr, 0.24

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mole) was added to the Grignard solution, then the solution was refluxed overnight. Acid hydrolysis gave 37.5 gr of *m*-methoxyvalerophenone (81% yield); $^1\text{H-NMR}$ (CDCl_3) δ 7.50-7.00 (m, 4H, Ar-H's), 3.85 (s, 3H), 2.90 (t, 2H), 2.00-1.20 (m, 4H), 0.98 (t, 3H). *m*-Methoxyvalerophenone (32.5 gr) and 50 gr of AlCl_3 in 160 ml benzene were heated on a steam bath for 3 hr.¹⁰⁶ After cooling down, the dark brown solution was hydrolyzed with cold HCl-water. The benzene layer was extracted with NaOH solution. The aqueous layer was acidified with conc. HCl. The resulting oil was extracted with ether. The ether solution was washed twice with saturated NaCl solution, dried over MgSO_4 , then ether was evaporated. The final slightly yellow solid was identified as *m*-hydroxyvalerophenone and used without further purification; m.p. = 65-67 °C; $^1\text{H-NMR}$ (FT-80, CDCl_3) δ 7.61-7.05 (m, 4H), 2.98 (t, 2H), 1.84-1.29 (m, 4H), 0.97 (t, 3H); MS (m/e), 178 (M^+), 136, 121 (base), 108, 93, 77, 65; IR spectrum (CCl_4), 3450 (br, OH), 2975, 1675 (C=O), 1600, 1450, 1275 cm^{-1} .

Meta-alkenoxyvalerophenones : The corresponding bromides, *m*-hydroxyvalerophenone, and potassium carbonate in dry acetone were refluxed overnight. The products were purified by vacuum distillation.

3'-(3-Buten-1-oxy)valerophenone : b.p. = 114.5-116 °C (0.1 Torr); $^1\text{H-NMR}$ (CDCl_3), δ 7.52-7.45 (m, 2H), 7.32 (m, 1H), 7.07 (m, 1H), 5.87 (m, 1H, -CH=C), 5.19-5.07 (m, 2H, C=CH₂), 4.04 (t, 2H, -CH₂O-), 2.92 (t, 2H, -CH₂C=O), 2.53 (m, 2H),

1.69 (m, 2H), 1.35 (m, 2H), 0.96 (t, 3H); MS (m/e), 232 (M^+), 190, 175 (base), 162, 146, 136, 121, 108, 55; IR (CCl_4), 2960, 1675 (C=O), 1590, 1250 cm^{-1} .

3'-(4-Penten-1-oxy)valerophenone : b.p. = 124-126 °C (0.1 Torr); 1H -NMR ($CDCl_3$), δ 7.51-7.44 (m, 2H), 7.32 (m, 1H), 7.06 (m, 1H), 5.95-5.75 (m, 1H, -CH=C), 5.08-5.00 (m, 2H, C=CH₂), 4.00 (t, 2H, CH₂O), 2.92 (t, 2H, CH₂C=O), 2.21 (m, 2H), 1.88 (m, 2H), 1.69 (m, 2H), 1.38 (m, 2H), 0.93 (t, 3H); MS (m/e), 246 (M^+), 204, 189, 147, 136, 121 (base), 93, 55; IR (CCl_4), 2950, 1675 (C=O), 1580, 1430, 1250 cm^{-1} .

3'-(4-Methyl-3-Penten-1-oxy)valerophenone : b.p. = 135-135.6 °C (0.1 Torr); 1H -NMR ($CDCl_3$), δ 7.52-7.45 (m, 2H), 7.32 (m, 1H), 7.06 (m, 1H), 5.25-5.15 (m, 1H, -CH=C), 3.96 (t, 2H, -OCH₂), 2.96 (t, 2H, CH₂C=O), 2.47 (m, 2H), 1.75-1.65 (m, 2H), 1.71 (s, 3H), 1.65 (s, 3H), 1.38 (m, 2H), 0.93 (t, 3H); MS (m/e), 260, 203, 178, 121 83 (base), 55; IR (CCl_4), 2960, 2925, 2875, 1685 (C=O), 1580, 1430, 1250 cm^{-1} .

3'-(5-Methyl-4-hexen-1-oxy)valerophenone : b.p. = 143-145 °C (0.1 Torr); 1H -NMR ($CDCl_3$), δ 7.52-7.44 (m, 2H), 7.32 (m, 1H), 7.06 (m, 1H), 5.17-5.08 (m, 1H, -CH=C), 3.97 (t, 2H, CH₂O), 2.92 (t, 2H, CH₂C=O), 2.15 (m, 2H), 1.88-1.75 (m, 2H), 1.75-1.65 (m, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.38 (m, 2H), 0.93 (t, 3H); MS (m/e), 274 (M^+), 217, 179, 161, 136, 121, 96 (base), 81, 69, 55; IR (CCl_4), 2910, 2880, 1680 (C=O), 1575, 1430, 1250 cm^{-1} .

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γ -Vinylbutyrophenones and δ -vinylvalerophenones : The following general method was used. To the Grignard solution of a alkenyl bromide in THF, were added equimolar amount of benzonitrile, then the solution was refluxed overnight. After acid hydrolysis, acidic aqueous solution was heated on a steam bath for 2 hr, cooled, then extracted with ether. The ether solution was combined with that collected during acid hydrolysis. After the evaporation of ether, the ketone was purified by vacuum distillation.

1-Phenyl-5-hexen-1-one : b.p. 80-80.5 °C (0.1 Torr); ^1H -NMR (250 MHz, CDCl_3) δ 7.92 (d, 2H), 7.53-7.40 (m, 3H), 5.90-5.70 (m, 1H), 5.06-4.95 (m, 2H), 2.96 (t, 2H), 2.14 (m, 2H), 1.83 (m, 2H); MS (70 eV, m/e), 174 (M^+), 120, 105 (base), 77, 51; IR (CCl_4), 3065, 2940, 1675 ($\text{C}=\text{O}$) cm^{-1} ; UV (heptane), 238.2 (12400), 278.2 (940), 286.2 (740), 323.2 nm (47).

cis-1-Phenyl-5-octen-1-one : b.p. 103-105 °C (0.5 Torr); ^1H -NMR (250 MHz, CDCl_3) δ 7.93 (d, 2H), 7.54-7.40 (m, 3H), 5.36 (m, 2H), 2.95 (t, 2H), 2.11 (m, 2H), 2.05 (m, 2H), 1.78 (m, 2H), 0.92 (t, 3H); I.R. (CCl_4), 3075 (aromatic C-H), 3010, 2975, 2940 (aliphatic C-H's), 1685 ($\text{C}=\text{O}$), 1450, 1225, 680 cm^{-1} ; MS (70 eV, m/e), 202 (M^+), 120, 105 (base), 77, 51, 44; UV (heptane), 237.8 (4900), 278.6 (330), 321.6 nm (36).

1-Phenyl-6-methyl-5-hepten-1-one : b.p. 83-85 °C (0.1 Torr); ^1H -NMR (FT-80, CDCl_3) δ 7.82 (m, 2H), 7.45 (m, 3H), 5.10 (m, 1H), 2.87 (t, 3H), 1.98 (m, 4H), 1.70 (s, 3H), 1.52

(s, 3H); MS (70 eV, m/e), 202 (M^+), 120, 105, 82 (base), 77, 67, 51; IR (CCl_4), 2970, 2930, 1665 (C=O) cm^{-1} ; UV (heptane), 238.0 (12200), 277.6 (900), 285.8 (720), 324.0 nm (48).

cis-1-Phenyl-6-nonen-1-one : b.p. 113-115 °C (0.= Torr); 1H -NMR (FT-80, $CDCl_3$) δ 7.85 (m, 2H), 7.45 (m, 2H), 5.32 (m, 2H), 2.85 (t, 3H), 2.05 (m, 4H), 1.75 (m, 4H), 0.97 (t, 3H); MS (70 eV, m/e), 216 (M^+), 133, 120, 105 (base), 94, 77, 67, 51; IR (CCl_4), 2925, 1685 (C=O) cm^{-1} ; UV (heptane), 238.0 (12600), 278.0 (970), 286.0 (780), 324.2 nm (48).

5. Equipment and Procedures

a. Photochemical Glasswares - All pipettes and volumetric flasks were Class A type. This glassware was rinsed with acetone three times, then with water, and boiled in a solution of Alconox laboratory detergent in distilled water for 12 hr. The glassware was rinsed with distilled water, and soaked in boiling distilled water for 12-24 hr. This process was repeated at least three times. This method was also used for syringes and the Pyrex test tubes used for irradiations. After the final distilled water rinse, the glassware was dried in an oven reserved specially for photochemical glassware at 150 °C.

Ampoules used for irradiation were made by heating the previously cleaned Pyrex tubes (13 x 100 mm) approximately 2.5

cm from the top with an oxygen-natural gas torch and drawing them out to a uniform 15 cm length.

b. Sample Preparations - All solution were prepared by either direct measurement into volumetric flasks or diluting a stock solution. A constant volumn (2.8 ml) of the final solution were transfered via syringe into each ampoule. Usually standards used for analyses were weighed directly into the ketone stock solution flasks (internal standards). Or a constant volume of external standard solutions were added to each solutions after irradiation.

c. Degassing Procedures - Sample tubes were attached to a vacuum line (10^{-4} torr) equipped with a diffusion pump. When the excited triplets have longer lightimes (μ s scale), a diffusion pump was used. These tubes were connected on a circular manifold equipped with twelve vacuum stopcocks each fitted with one hole rubber (size 00). The sample tubes were slowly frozen in liquid nitrogen bath from the bottom to the top and evacuated for 5-10 min. The vacuum was disconnected and the tubes allowed to thaw at room temperature. This freeze-pump-thaw cycle was repeated three times. After the final cycle, the tubes were frozen, evacuated for 5 min, and sealed with an oxygen-natural gas torch while still under vacuum.

d. Irradiation Procedures - All samples for lifetime measurement or quantum yield measurement were irradiated in

parallel with actinometer solutions in a Merry-Go-Round apparatus immersed in a water bath at approximately 25 °C. A water cooled Hanovia medium pressure mercury lamp was used as the irradiation source. An alkaline potassium chromate solution (0.002 M K_2CrO_4 in 1% aqueous potassium carbonate) was used to isolate the 313 nm emission band. A Corning 7-83 filter was used to isolate the 365 nm emission band.

Preparative scale photolyses were performed using a Hanovia medium pressure mercury lamp filtered through Pyrex. Samples (200 mg) dissolved in 250 ml spectral grade benzene were irradiated at tap water temperature under a steady stream of argon.

Photolyses for direct 1H -NMR measurement were performed in a water bath with 313 nm. Samples (15 mg) were dissolved in 2 ml benzene- d_6 , bubbled with argon before irradiation.

e. Analysis Procedures - All GLC analyses were performed on either a Varian Model 1200 or 1400 Gas Chromatogram with a flame ionization detector. Gas chromatograms were connected to either Infotronics CRS 309 Digital Integrator or Hewlett-Packard Model 3393 A Integrator.

Analyses by HPLC were performed on a Beckman Model 332 Gradient Liquid Chromatograph System equipped with a Perkin-Elmer LC-75 Ultraviolet-Visible Detector and DuPont 860 Column Compartment. An Altex Ultrasphere Si Absorption Phase column were used for separations. Solvents used were either HPLC Grade or Spectral Grade and were filtered through a 0.45 μm

Nylon 66 membrane prior to use. The UV detecting system was connected to a Hewlett-Packard Model 3380 Integrator.

For gas chromatography, all samples were introduced by on-column injection with a carrier gas (nitrogen) flow rate of 40 ml/min. The following 1/8" o.d. aluminum columns were used -

- Column #1 - 6' 3% QF-1 on Chromsorb G
- Column #2 - 6' 3% QF-1 with 2% KOH on Chromsorb G
- Column #3 - 5' 5% SE-30 on Chromsorb G
- Column #4 - 25' Fused Silica Megabore Column

The concentration of the photoproducts was calculated from the following equation.

$$[\text{photo}] = (\text{R.F.}) \times [\text{std}] \times \frac{A_{\text{photo}}}{A_{\text{std}}}$$

Response factors for each of the photoproducts and their respective internal standard were obtained by gas chromatography and calculated from the following equation:

$$\text{R.F.} = \frac{A_{\text{std}}}{A_{\text{photo}}} \times \frac{\text{moles}_{\text{photo}}}{\text{moles}_{\text{std}}}$$

When a photoproduct isolated was not enough to measure the response factor, the following calculation was applied:

$$\text{R.F.} = \frac{(\# \text{ of C's} + 1/2(\# \text{ of C-O bonds}))_{\text{std}}}{(\# \text{ of C's} + 1/2(\# \text{ of C-O bonds}))_{\text{photo}}}$$

For all HPLC analyses, the first equation was used. The response factors are summarized in Table 23 and 24.

f. Calculation of Quantum Yields - The amount of photons absorbed by samples was determined by valerophenone actinometry. A degassed 0.10 M valerophenone in benzene was irradiated in parallel with the samples to be analyzed. After completion of the irradiation, valerophenone solution was analyzed for acetophenone, using the same equation as that for ketones.

The quantum yield for the photoproduct formation was calculated from the acetophenone concentration knowing that the quantum yield for valerophenone is 0.33.

$$\Phi = \frac{[\text{prod}]}{[\text{AP}]} \times 0.33$$

B. Isolation and Identification of Photoproducts

In general, photoproducts were obtained by a large scale photolysis of 0.01 to 0.1 M solutions of a ketone in spectral grade benzene or acetonitrile under argon atmosphere. The conversion was monitored by an analytical GC. A medium pressure Hanovia mercury vapor lamp was used as a light source. A pyrex filter was used to filter out the light below 295 nm.

Identification of the primary photoproduct from ortho-(3-methyl-3-buten-1-oxy)acetophenone was based on ^1H -NMR, homo-

Table 23. Gas chromatographic response factors for various photoproducts.

Standard/Photoproduct	conditions ^a	R.F.
C ₁₆ /Acetophenone	#1, 140°C	1.92
C ₈ Bz/4-valeryl-cyclooctatriene ^b	#2, 190°C	0.938
C ₇ Bz/3-valeryl-cyclooctatriene ^c	#2, 190°C	1.077
C ₇ Bz/3-valeryl-1-Me-cyclooctatriene ^d	#2, 192°C	0.966
C ₇ Bz/1-actyl-hexadiene ^e	#4, 160°C	0.933
C ₅ Bz/m-(3-butenoxy) acetophenone	#4, 160°C	1.200
C ₁₀ Bz/m-(4-Me-3-pentenoxo) acetophenone	#4, 180°C	1.289

^acolumns and temperatures

^b4-valeryl-11-oxabicyclo[6.3.0]undec-1,3,5-triene.

^c3-valeryl-9-oxabicyclo[6.3.0]undec-3,5,7-triene.

^d3-valeryl-1-methyl-9-oxabicyclo[6.3.0]undec-3,5,7-triene.

^e1-acetyl-2,2-dimethyl-6-oxatricyclo[5.4.0.0^{3,7}]undec-8,10-diene.

Talbe 24. HPLC response factors for various photoproducts.

Standard/Photoproducts	R.F. ^a
C ₁ Bz/p-methoxyacetophenone (p-AP0)	0.04868
C ₁ Bz/p-AP ₁ 1	0.04485
C ₁ Bz/p-AP ₁ 2	0.04352
C ₁ Bz/p-AP ₁ 3	0.03804
C ₁ Bz/p-AP ₂ 1	0.0412
C ₁ Bz/p-AP ₂ 2	0.0403
C ₁ Bz/p-AP ₃ 1, p-AP ₄ 1, p-AP ₉ 1, p-AP ₃ 3, p-AP ₃ 2	0.0412

^aUltrasphere Si column, hexane/ethyl acetate (97/3), @ 270 nm.

decoupling, NOE technique, ^{13}C -NMR, partially decoupled ^{13}C -NMR, IR, GC-MS, and UV-Visible spectra. Direct products from other ketones were identified basically from ^1H -NMR spectra and all spectral data of the primary photoproduct from ortho-(3-methyl-3-buten-1-oxy)acetophenone were used as references. The attempt for purifying photoproduct resulted in the thermal rearrangement and a preparative TLC gave the same rearranged products as those from a preparative GC. Usually the major rearranged products were cyclooctatrienes. The preparative GC (Varian Model 920) was set as injecting port temperature of 180 to 200 $^{\circ}\text{C}$, the detector temperature of 200 to 210 $^{\circ}\text{C}$, and the oven temperature of 160 to 180 $^{\circ}\text{C}$.

To see the direct photoproducts, about 0.05-0.1 M of alkenoxyphenyl ketones in benzene- d_6 were bubbled in small test tubes with argon for 5-10 min, then irradiated outside the 313-nm filter solution. The ^1H -NMR were taken repeatedly after a certain time interval irradiation (2-12 hours). The spectra showed one major photoproduct in most cases.

The sample solutions for the time-based UV-Visible spectra were prepared by adding a certain volume of stock solution into an UV cell and diluting with 3 ml of solvent. Then the septum-capped cell was bubbled with dried argon at least 10 min. Usually, the changes in the spectra were detectable within 30 sec.

Structural assignments were based on ^1H -NMR and ^{13}C -NMR, Infrared spectroscopy, and mass spectroscopy. ^1H -NMR spectra were recorded on either a Varian T-60 NMR Spectrometer, a Varian CFT-20 NMR Spectrometer (80 MHz), or a Bruker WM-250

Fourier Transform NMR Spectrometer. ^{13}C -NMR spectra were recorded on the Bruker WM-250 instrument (62.9 MHz). All spectra were calibrated using either tetramethylsilane ($\delta = 0.0$ ppm) or solvents (chloroform, δ 7.24 ppm; benzene, δ 7.15 ppm) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 237 B Grating Infrared Spectrophotometer. Mass spectra were recorded on a Finnigan 4000 GC/MS using the direct inlet mode. This instrument was operated by Mr. Ernest A. Oliver or Dr. Rick Olson. Ultraviolet-Visible absorption were recorded on a Varian Carey 219 Spectrophotometer or a Shimadzu UV-160 Spectrophotometer. Melting points were recorded on a Thomas Hoover Capillary Melting Point Apparatus and are not corrected.

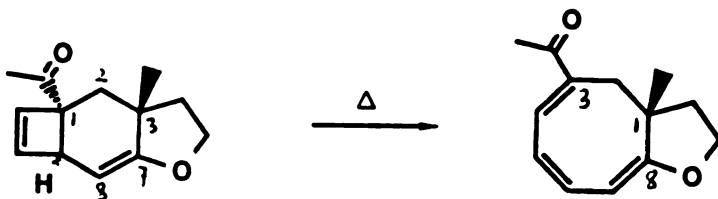
2'-(3-Methyl-3-buten-1-oxy)acetophenone, (Q-AP₂) : 5-10 mg of the ketone in 2 ml of benzene-d₆ was irradiated and its ^1H -NMR spectra were taken every two hours. Two photoproducts were observed and the ratio was 7:1 from the integration of ^1H -NMR spectrum. The major product was characterized as 1-acetyl-3-methyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-diene: ^1H -NMR (250 MHz, C₆D₆) δ 6.04 (dd, 1H, J = 0.9, 2.8), 5.81 (d, 1H, J = 2.8), 4.98 (d, 1H, J = 6.6), 3.77 (m, 2H), 3.32 (dd, 1H, J = 0.9, 6.6), 1.90 (d, 2H), 1.85 (s, 3H), 1.38 (dt, 1H, J = 11, 9.5), 1.25 (dd, 1H, J = 11, 4.1), 1.02 (s, 3H); ^{13}C -NMR (62.9 MHz, C₆D₆) δ 207.9 (s), 163.9 (s), 144.8 (d, J = 130.7 Hz), 139.6 (d, 128.1), 90.8 (d, J = 111.8), 67.3 (t, J = 92.0), 63.2 (s), 46.3 (d, J = 83.8), 41.7 (t, J = 55.5), 40.0 (t, J = 60.1), 39.5 (s), 25.3 (q, J = 61.0), 24.0 (q, J = 50.0); MS,

m/e 204 (M^+), 189, 161, 136, 121, 105, 91, 43 (base); FT-IR (CHCl_3) 2995, 2961, 2930, 2899 (m, aliphatic C-H stretching), 1688.5 (s, carbonyl), 1665 (w, C=C), 1160 (s) cm^{-1} ; UV-Visible (CH_3CN) 295 nm (200)

Thermal rearrangement of the tricyclic product in a preparative GC gave 6-acetyl-8-methyl-11-oxabicyclo[6.3.0]undec-1,3,5-triene: $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.13 (d, 1H, $J = 5.7$), 6.12 (dd, 1H, $J = 12.5, 7.7$), 5.84 (dd, 1H, $J = 12.8, 5.7$), 5.17 (d, 1H, $J = 7.7$), 4.10 (dd, 2H, $J = 3.2$), 2.91 (d, 1H, $J = 13.2$), 2.45 (d, 1H, $J = 13.2$), 2.08 (td, 1H, $J = 10.4$), 1.87 (s, 3H), 1.85 (td, 1H, $J = 3.2$), 1.02 (s, 3H); MS, m/e 204 (M^+), 189, 136, 121, 105, 43 (base); UV-Visible (hexane) 237 nm (19,000), 374 nm (4,400).

Irradiation (313 or 365 nm) of the above cyclooctatriene (ca. 0.01 M) in benzene- d_6 gave the identical tricyclic product on $^1\text{H-NMR}$ spectra. Also the unknown minor product was observed: $^1\text{H-NMR}$ (C_6D_6), δ 6.31 (d of d, 1H, $J = 4.8, 2.9$ Hz), 6.07 (d of d, 1H, $J = 2.9, 1.5$ Hz), 5.75 (d, 1H, $J = 2.9$ Hz), 3.35 (d, 1H, $J = 5.5$ Hz), 1.91 (s, 3H), 0.74 (s, 3H), others not determined.

Irradiation of 15 mg of α -AP₂2 in 250 ml benzene at >295 nm for 30 min gave both the cyclooctatriene and the cyclobutene product. (see Fig. 26)



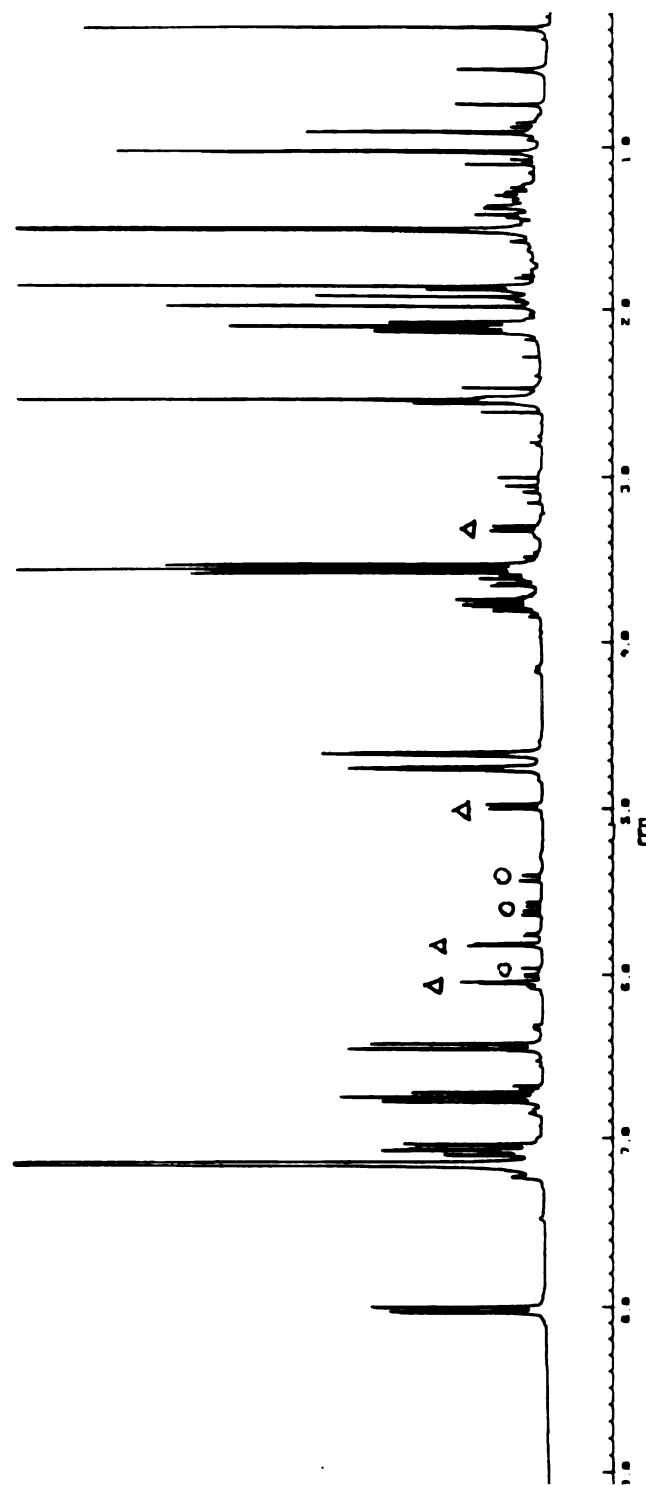
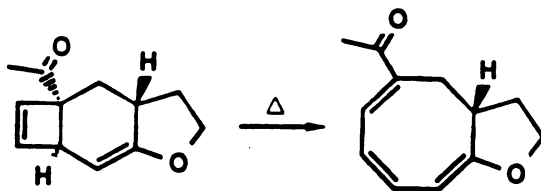


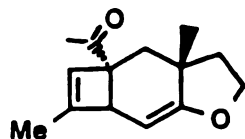
Figure 26. The ^1H -NMR spectrum of ϱ -AP₂₂ of 313 nm irradiation (15 mg in 250 ml of benzene); (Δ) the cyclobutene, (O) the cyclooctatriene.

2'-(3-Buten-1-oxy)acetophenone, (α -AP₂1) : 10-20 mg of the ketone in argon-bubbled benzene-d₆ was irradiated at 313 nm. A single product was detected on the ¹H-NMR spectrum after 3-4 hrs. Continuous irradiation (overnight) could not give 100% conversion but ca. 70-80% conversion. The direct photoproduct was 1-acetyl-6-oxa-tricyclo[7.2.0.0^{3,7}]undec-7,10-diene: ¹H-NMR (250 MHz, C₆D₆) δ 5.86 (d, 1H, J = 2.8 Hz), 5.78 (d, 1H, J = 2.8), 4.96 (d, 1H, J = 6.6), 3.78 (t, 1H, J = 8.5), 3.50 (dq, 1H, J = 8.5, 5.7), 3.26 (d, 1H, J = 6.6), 2.09 (m, 1H), 1.84 (s, 3H), 1.78 (, 1H, J = 5.1), 1.48 (t, 1H, J = 13), 1.46 (t, 1H, J = 12.5), 1.21 (m, 1H, J = 8.5, 11.5). After through a preparative GC column (SE-30) at 170-180 °C, the tricyclo product underwent thermal rearrangement to give yellow 6-acethyl-11-oxabicyclo[6.3.0]undec-1,3,5-triene: ¹H-NMR (250 MHz, CDCl₃) δ 7.13 (d, 1H, J = 6.2), 6.06 (dd, 1H, J = 13, 8.8), 5.75 (dd, 1H, J = 13, 6.2), 5.34 (dd, 1H, J = 8.8, 1.9), 4.13 (dt, 1H, J = 2.5, 8.1), 4.02 (dt, 1H, J = 5.7, 11.5), 3.04 (dd, 1H, J = 1.9, 13.4), 2.73 (m, 1H, J = 8.3), 2.23 (dd, 1H, J = 13.4, 8.3), 1.85 (m, 1H, J = 8.1).



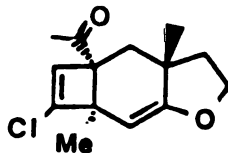
2'-(3-Methyl-3-buten-1-oxy)-5'-methylacetophenone : The starting ketone in the argon-bubbled benzene-d₆ in a test tube was irradiated at 313 nm and yielded a photoproduct. After >95 % conversion checked by ¹H-NMR spectra, the solvent was

evaporated. The photoproduct was 1-acetyl-3,10-dimethyl-6-oxatricyclo[7.2.0^{3,7}]undec-7,10-diene: ¹H-NMR (250 MHz, C₆D₆) δ 5.49 (d, 1H, J = 1.5), 4.99 (d, 1H, J = 6.7), 3.78 (m, 2H), 3.16 (d, 1H, J = 6.7), 1.93 (d, 1H, J = 14.9), 1.88 (s, 3H), 1.84 (d, 1H, J = 14.9), 1.42 (s, 3H), 1.34 (m, 2H), 1.01 (s, 3H); MS (70 eV), m/e 218 (M⁺), 203, 175, 163, 150, 135, 119, 108, 91, 77, 69, 55, 43 (base).



2'-(3-Methyl-3-buten-1-oxy)-5'-chloro-4'-methylacetophenone :

Irradiation (313 nm) of the ketone in benzene-d₆ gave one product which was monitored by NMR. The product was identified as 1-acetyl-10-chloro-3,9-dimethyl-6-oxatricyclo[7.2.0^{2,7}.0]undec-7,10-diene: ¹H-NMR (250 MHz, C₆D₆) δ 6.71 (s, 1H), 5.15 (s, 1H), 3.64 (t, 1H, J = 8.7), 3.52 (m, 1H, J = 5.5, 8.7), 2.98 (d, 1H, J = 13.1), 2.25 (d, 1H, J = 13.1), 1.99 (ABX, 1H, J = 12.9, 3.0), 1.91 (s, 3H), 1.80 (s, 3H), 1.26 (ABX, 1H, J = 12.9, 5.5), 0.87 (s, 3H); MS (70 eV), m/e 254:252 (1:3 ratio, M⁺), 237, 217, 209, 184, 169, 153, 100, 91, 77, 69, 55, 43 (base); UV (CH₃CN), no major absorption above 300 nm.



2'-(cis-3-Hexen-1-oxy)acetophenone (o-AP₂cis) : Irradiation (313 or >295 nm) of the ketone in benzene gave two photo-products. One of these was identified as a tricyclo-[7.2.0^{3,7}.0]undec-7,10-diene. Major product was not identified yet. But after column chromatography, the major product converted to a cycloocta- triene.

1-Acetyl-2-ethyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-diene:

¹H-NMR (C₆D₆), δ 6.04 (d, 1H, J = 2.9 Hz), 5.89 (d, 1H, J = 2.9 Hz), 4.92 (d of d, 1H), 3.07 (d, 1H) ppm, others not determined.

The major product: ¹H-NMR (C₆D₆), δ 6.32 (d, 1H, J = 5.1 Hz), 6.00 (s, 1H), 3.55-4.98 (m, 2H), 3.37 (d, 1H, J = 5.1 Hz), 3.18 (m, 1H), 1.94 (s, 3H), 1.85-1.95 (m, 2H), 1.60-1.70 (m, 2H), 1.35-1.50 (m, 2H), 1.00 (t, 3H); MS, m/e 218 (M⁺), 203, 189, 175, 147, 133, 120, 105, 91, 77, 65, 55.

The rearranged product from the major photoproduct; ¹H-NMR (C₆D₆), δ 6.62 (d, 1H, J = 5.3 Hz), 5.98 (d of d, 1H, J = 5.7, 11.1 Hz), 5.60 (d of d, 1H, J = 5.3, 11.1 Hz), 5.48 (d, 1H, J = 5.7 Hz), 3.85-3.55 (m, 2H), 1.92 (s, 3H), others not determined; MS, m/e 218 (M⁺), 203, 189, 175, 147, 133, 120, 105, 91, 77; UV-Visible (heptane), λ_{max} 335, 237 nm.

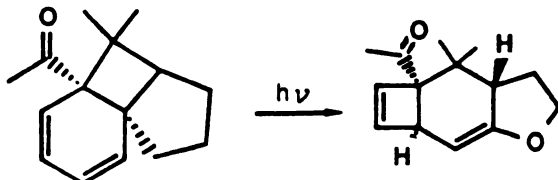
2'-(4-Methyl-3-penten-1-oxy)acetophenone, (o-AP₂3) : This ketone gave initially a cyclohexadiene derivative (30-40 %) on

313 or >295-nm irradiation, which converted to a cyclobutene derivative on prolonged irradiation. The cyclohexadiene (up to 80 % purity) was isolated by column chromatography (silica gel, hexane/ether (99/1)).

1-Acetyl-2,2-dimethyl-6-oxa-tricyclo[5.4.0.0^{3,7}]undec-8,10-diene: ¹H-NMR (250 MHz, C₆D₆) δ 5.69 (dd, 1H, J = 9.6, 5.6), 5.53 (dd, 1H, J = 9.8, 5.6), 5.43 (d, 1H, J = 9.6), 5.34 (d, 1H, J = 9.8), 3.68 (m 2H), 2.47 (dd, 1H, J = 8.5, 1.8), 2.31 (s, 3H), 1.52-1.60 (m, 1H, J = 1.8), 1.34-1.45 (m, 1H, J = 8.5), 1.25 (s, 3H), 1.19 (s, 3H).

1-Acetyl-2,2-dimethyl-6-oxatricyclo[7.2.0.0^{3,7}]undec-7,10-diene: ¹H-NMR (250 MHz, C₆D₆) δ 6.00 (d, 1H, J = 2.8 Hz), 5.76 (d, 1H, J = 2.8), 4.97 (dd, 1H, J = 2.7, 6.4), 3.79 (dt, 1H, J = 2.4, 8.5), 3.57 (m, 1H, J = 8.5), 3.54 (d, 1H, J = 6.4), 2.35 (dt, 1H, J = 2.7, 10.1), 1.88 (s, 3H), 1.37 (m, 2H), 0.91 (s, 3H), 0.70 (s, 3H). Also two small singlets appeared at 0.84 and 0.76 ppm and were considered to come from a isomer; MS (70 eV, m/e), 218 (M⁺), 203, 185, 175, 161, 147, 133, 120, 105, 91, 83, 55, 43 (base).

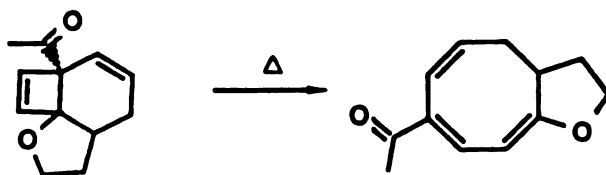
After the cyclobutene was heated at 130 °C on an oil-bath under argon gas for 45 min, it was dissolved in benzene-d₆. The ¹H-NMR spectrum was the same as that of the cyclohexadiene.



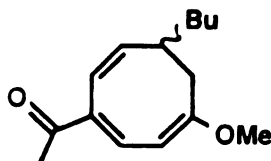
4'-(3-Buten-1-oxy)acetophenone, (p-AP₂1) : ¹H-NMR spectrum was taken from the direct photoproduct, which was derived from the 313-nm irradiation in benzene-d₆. Some precipitate were formed and filtered off with hexane-ether solvent through a glass filter filled with silica gel in a short time period. 1-Acetyl-8-oxatricyclo[7.2.0.0^{5,9}] undec-2,10-diene: ¹H-NMR (250 MHz, C₆D₆) δ 6.06 (d, 1H, J = 2.7), 5.85 (d, 1H, J = 2.7), 5.83 (d, 1H, J = 11.1), 5.59 (m, 1H, J = 11.1), 3.64 (dt, 1H, J = 2.7, 8.0), 3.51 (m, 1H, J = 8.0), 2.09 (s, 3H), 1.86 (m, 3H), 1.78 (m, 1H), 1.34 (m, 1H); ¹³C-NMR (62.9 MHz, CDCl₃) δ 210.3, 139.0, 138.4, 126.3, 125.8, 68.9, 68.6, 66.7, 39.5, 28.7, 28.0, 24.5; MS (70 eV) m/e 190 (M⁺), 175, 162, 147, 129, 121, 105, 91, 77, 55, 43 (base).

The product collected by prep GC was identified as 4-acetyl-11-oxa-bicyclo[6.3.0]undeca-1,3,5-triene: ¹H-NMR (250 MHz, CDCl₃) δ 7.00 (d, 1H, J = 6.8), 6.27 (d, 1H, J = 12.5), 5.92 (q, 1H, J = 12.5, 6.8), 5.40 (d, 1H, J = 6.8), 4.24 (m, 1H, J = 6.8), 4.16 (m, 1H, J = 6.8), 3.06 (m, 1H, J = 6.3), 2.38 (s, 3H), 2.29-2.50 (m, 2H, J = 6.8, 6.3), 2.13 (m, 1H, J = 6.3), 1.83 (m, 1H, J = 6.3); ¹³C-NMR (62.9 MHz, CDCl₃) δ 199.3, 170.5, 144.6, 137.8, 131.6, 125.1, 96.1, 69.3, 40.1, 31.3, 30.9, 26.4.

From the valerophenone derivative, another product was collected by preparative GC. This product has three vinyl protons: ¹H-NMR (250 MHz, CDCl₃) δ 7.12 (d, 1H, J = 5.2), 6.07 (d, 1H, J = 12.6), 5.93 (dd, 1H, J = 5.2, 12.6), 4.23 (t, 2H), others not determined.



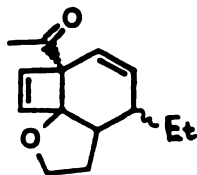
4'-Methoxyacetophenone with 1-hexene : p-Methoxyacetophenone (0.1 gr) in 1-hexene (10 ml) was irradiated with 313 nm light after bubbling with argon for 10 min. The conversion was monitored on GC. After about 10 % conversion, a product was collected from a preparative GC. The product was not 100 % pure, but clearly four vinyl protons were observed on $^1\text{H-NMR}$ spectrum: $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.08 (d, 1H, $J = 5.2$ Hz), 5.82 (dd, 1H, $J = 12.3, 4.6$), 5.67 (d, 1H, $J = 12.3$), 5.19 (d, 1H, $J = 5.2$), 3.72 (s, 3H), 2.38 (s, 3H); MS (70 eV), m/e 234 (M^+), 219, 203, 191, 177, 161, 135 (base), 121, 91, 77, 58; UV-Visible (heptane), $\lambda_{\text{max}} = 312$ nm.



4'-(cis-3-hexen-1-oxy)valerophenone, (p-VP₂cis) : The efficient photoisomerization of the cis ketone gave the trans-derivative. After 7-8 hr irradiation, HPLC analyses showed that the solution reached an equilibrium state which has about 85 % of the trans and 15 % of the cis ketone. The trans ketone has the following spectroscopic data: $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.92 (d, 2H), 6.91 (d, 2H), 5.56 (m, 2H, $J = 15.7$ Hz), 4.02 (t, 2H), 2.86 (t, 2H), 2.48 (m, O-C-CH₂), 2.04 (m, C=C-CH₂),

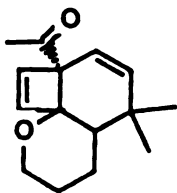
1.68 (m, 2H), 1.39 (m, 2H), 0.99 and 0.95 (2 t, each 3H); I.R. (CCl_4), 2970, 2940, 2890 (aliphatic C-H's), 1675 (C=O), 1600 (C=C), 1245, 1160 cm^{-1} .

The cis acetophenone derivative in benzene was irradiated with argon bubbling at >295 nm overnight and a product was observed on GC. It showed the vinyl proton peaks of a cyclobutene in ^1H -NMR spectrum; two doublets at 6.25 and 6.35 ppm with $J = 3$ Hz.



4'-(5-Methyl-4-hexen-1-oxy)acetophenone, (p-AP₃) : The initial product (<20 % conversion) was identified as 1-acetyl-4,4-dimethyl-9-oxatricyclo[8,2, 0,0^{5,10}]dodec-2,11-diene: ^1H -NMR (250 Mz, C_6D_6) δ 6.55 (d, 1H, $J = 3.1$ Hz), 6.34 (d, 1H, $J = 3.1$), 5.46 (d, 1H, $J = 10.2$), 5.40 (d, 1H, $J = 10.2$), 3.45 (m, 1H), 3.23 (m, 1H), 2.33 (s, 3H), 0.85 (s, 3H), 0.74 (s, 3H), others not determined.

Further irradiation gave a cyclooctatriene-like product which has four vinyl protons: ^1H -NMR $\delta(\text{C}_6\text{D}_6)$, 6.22 (d, 1H, $J = 7.7$ Hz), 6.01 (d of d, 1H, $J = 7.7, 6.0$ Hz), 5.77 (d, 1H, $J = 6.0$ Hz), 5.57 (d of d, 1H, $J = 6.0, 2.4$ Hz), 3.24 (d of t, 1H, $J = 2.4, 10.6$ Hz), 2.53 (s, 3H) ppm, others not determined.



4'-(3-buten-1-oxy)benzophenone : The benzophenone in benzene- d_6 in a small test tube was bubbled with dried argon and irradiated at 313 nm for 24 hr. The ^1H -NMR spectrum showed new peaks which correspond to a cyclobutene, but the conversion to the product was estimated to be less than 1 %. The new peaks; ^1H -NMR (250 MHz, C_6D_6), δ 6.14 (d, $J = 3$ Hz), 5.98 (d, $J = 3$ Hz), 5.85 (d, $J = 10.5$ Hz), others were not determined.

APPENDIX

The tables in this Appendix show the raw data from quantum yield measurements and Stern-Volmer quenching studies. Analysis conditions, concentrations of the materials used (ketones, internal & external standards, products, and actinometry), as well as other pertinent experimental conditions are also provided. In all cases, g.c. or HPLC peak area ratios are the average of at least two injections.

The following abbreviations are used for the actinometer and the standards;

ACP = acetophenone, VP = valerophenone,

MeBz = methyl benzoate, C4Bz = n-butyl benzoate,

C8Bz = n-octyl benzoate, CnBz = n-alkyl benzoate, etc.

TABLE 25. Quenching of the type II product formation from p-methoxyvalerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.

Run 1.^a

$k_q \tau = 3900$, $\Phi_{II} = 0.16^b$ HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], $10^{-4}M$	(Pr/St) _{area}	[p-MeO-ACP], $10^{-4}M$	Φ_o/Φ
0.0	.658	2.67	1.00
0.52	.592	2.40	1.14
1.3	.441	1.79	1.53
2.6	.356	1.45	1.89
5.2	.264	1.07	2.55
10.4	.131	0.53	5.15

^a [KETONE] = 0.24 M, [MeBz] = 0.00833 M, 313 nm, 15 min.

^b VP actinometer; [VP] = 0.11 M, [C16] = 0.0124 M, [ACP] = 0.000618 M.

Run 2.^a

$$k_q \tau = 4400, \quad \Phi_{II} = 0.12^b$$

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[p-MeO-ACP], 10 ⁻⁴ M	Φ_o/Φ
0.0	3.083	8.30	1.00
0.67	2.823	7.60	1.09
1.69	1.449	3.90	2.13
3.37	1.114	3.00	2.77
6.74	0.721	1.94	4.28
10.11	0.590	1.59	5.21
13.49	0.427	1.15	7.21

^a [KETONE] = 0.028 M, [MeBz] = 0.00553 M, 313 nm, 40 min.

^b VP actinometer; [ACP] = 0.00226 M

Run 3.^a

$$k_q \tau = 4100, \Phi_{II} = 0.19^b$$

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[p-MeO-ACP], 10 ⁻⁵ M	Φ_o/Φ
0.0	.807	25.56	1.00
1.93	.500	15.83	1.61
3.86	.357	11.31	2.26
7.71	.210	6.66	3.84
11.57	.142	4.50	5.68
15.43	.112	3.55	7.20

^a [KETONE] = 0.024 M, [MeBz] = 0.00651 M, 313 nm, 15 min.

^b VP actinometer; [ACP] = 0.000451 M

TABLE 26. Quenching of the type II product formation from p-methoxyvalerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$$k_q \tau = 4000, \quad \Phi_{II} = 0.18^b$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[p-MeO-ACP], 10 ⁻⁴ M	Φ_o/Φ
0.0	1.855	3.64	1.00
2.85	0.831	1.63	2.23
5.70	0.556	1.09	3.34
11.41	0.331	0.65	5.57
17.11	0.229	0.45	8.12
22.81	0.184	0.36	10.04

^a [KETONE] = 0.023 M, [MeBz] = 0.00403 M, 313 nm, 25 min.

^b VP actinometer; [ACP] = 0.000670 M.

TABLE 27. Quenching of the type II product formation from p-allyloxyvalerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 3700$, $\Phi_{II} = 0.145$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁵ M	Φ_o/Φ
0.0	1.972	45.9	1.00
2.75	1.211	28.2	1.63
5.49	0.644	15.0	3.07
10.99	0.420	9.77	4.70
16.48	0.282	6.56	7.00
21.97	0.201	5.05	9.09

^a [KETONE] = 0.014 M, [MeBz] = 0.00519 M, 313 nm, 30 min.

^b VP actinometer; [ACP] = 0.00107 M.

TABLE 28. Quenching of the type II product formation from p-allyloxyvalerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$k_q \tau = 2190$, $\Phi_{II} = 0.089$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁴ M	Φ_o/Φ
0.0	1.117	2.31	1.00
2.85	0.716	1.48	1.56
5.70	0.493	1.02	2.25
11.41	0.324	0.67	3.43
17.11	0.237	0.49	4.73
22.81	0.189	0.39	5.98

^a [KETONE] = 0.010 M, [MeBz] = 0.00461 M, 313 nm, 30 min.

^b VP actinometer; [ACP] = 0.00085 M.

TABLE 29. Quenching of the type II product formation from p-(2-methyl-2-propen-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25 °C.^a

$$k_q \tau = 3270, \quad \Phi_{II} = 0.14^b$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁴ M	Φ_o/Φ
0.0	2.710	6.12	1.00
2.75	1.355	3.06	2.01
5.49	0.987	2.23	2.74
10.99	0.584	1.32	4.64
16.48	0.434	0.98	6.24
21.97	0.328	0.74	8.23

^a [KETONE] = 0.014 M, [MeBz] = 0.00519 M, 313 nm, 45 min.

^b VP actinometer; [ACP] = 0.00144 M.

TABLE 30. Quenching of the type II product formation from p-(2-methyl-2-propen-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25 °C.^a

$$k_q \tau = 1460, \quad \Phi_{II} = 0.067^b$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁵ M	Φ_o/Φ
0.0	1.218	25.71	1.00
2.85	0.917	19.36	1.33
5.70	0.677	14.30	1.80
11.41	0.483	10.20	2.52
17.11	0.361	7.62	3.37
22.81	0.279	5.89	4.37

^a [KETONE] = 0.011 M, [MeBz] = 0.00485 M, 313 nm, 45 min.

^b VP actinometer; [ACP] = 0.00126 M.

TABLE 31. Quenching of the type II product formation from p-(3-methyl-2-buten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 1390$, $\Phi_{II} = 0.042$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁴ M	Φ_o/Φ
0.0	1.064	2.10	1.00
2.75	0.740	1.46	1.44
5.49	0.724	1.43	1.47
10.99	0.360	0.71	2.98
16.48	0.304	0.60	3.48
21.97	0.274	0.54	3.87

^a [KETONE] = 0.014 M, [MeBz] = 0.00519 M, 313 nm, 1hr.

^b VP actinometer; [ACP] = 0.00144 M.

TABLE 32. Quantum yield dependence on the concentration of p-allyloxyvalerophenone in acetonitrile at 25 °C.^a

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[KETONE]	[TYPE II] ^b	[ACP] ^{b,c}	Φ_{II}
.019	3.65	8.71	0.14
.0588	4.20	12.3	0.12
.0697	4.02	10.9	0.122
.0925	7.17	23.5	0.101
.173	4.58	23.5	0.064
.222	4.44	23.5	0.062
.251	1.68	10.9	0.051

^a several different runs were tabulated. ^b in 10⁻⁴ M.

^c the acetophenone concentration from the actinometry.

TABLE 33. Quantum yield dependence on the concentration of p-methallyloxyvalerophenone in acetonitrile at 25 °C.^a

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[KETONE]	[TYPE II], 10 ⁻⁴	[ACP] ^b , 10 ⁻³	Φ_{II}
.0178	3.72	1.35	0.091
.034	5.67	3.00	0.062
.054	4.44	3.00	0.049
.095	3.99	3.00	0.044
.122	3.06	3.00	0.034

^a several different runs were tabulated.

^b the acetophenone concentration from the actinometry.

TABLE 34. Quantum yield dependence on the concentration of p-(3-methyl-2-buten-1-oxy)valerophenone in acetonitrile at 25 °C.^a

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[KETONE]	[TYPE II], 10 ⁻⁴	[ACP] ^b , 10 ⁻³	Φ_{II}
.0087	2.12	1.35	0.052
.0140	1.81	1.53	0.039
.0413	2.68	4.20	0.021
.0723	2.10	4.20	0.0165
.0929	1.51	4.20	0.012

^a Several different runs were tabulated.

^b the acetophenone concentration from the actinometry.

TABLE 35. Quenching of product formation from p-(3-buten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 109$ $\Phi_{II} = 0.0032^b$ HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	A _{cyclo} /A _{st} ^c	A _{II} /A _{st}	Φ_o/Φ
0.0	.0599	0.212	1.00
1.93	.0572	0.208	1.02
3.86	.0572	0.202	1.05
7.71	.0555	0.196	1.08
15.43	.0514	0.180	1.17

^a [KETONE] = 0.019 M, [MeBz] = 0.00651 M, 313 nm, 1 hr.

^b VP actinometer; [ACP] = 0.00190 M. ^c Area ratio of (cycloadduct/MeBz).

TABLE 36. Quenching of the cycloaddition product formation from p-(3-buten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 116$, $\Phi_{II} = 0.028^b$ GC analysis: 5' SE-30 column
190°C

[diene], 10 ⁻² M	(Pr/St) _{area}	[adduct], 10 ⁻⁴ M	Φ_o/Φ
0.0	0.625	7.03	1.00
0.70	0.354	3.99	1.76
1.40	0.224	2.52	2.79
2.10	0.207	2.33	3.02
2.79	0.141	1.59	4.44

^a [KETONE] = 0.014 M, [C8Bz] = 0.00120 M, 313 nm, 5 hr.

^b VP actinometer; [ACP]_{total} = 0.00825 M.

TABLE 37. Quenching of the type II product formation from p-(4-penten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 2050$, $\Phi_{II} = 0.062$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁴ M	Φ_o/Φ
0.0	1.971	3.76	1.00
0.65	1.761	3.36	1.12
1.62	1.646	3.14	1.20
3.25	1.242	2.37	1.59
6.49	0.875	1.67	2.26
9.74	0.661	1.26	2.98

^a [KETONE] = 0.010 M, [MeBz] = 0.00463 M, 313 nm, 30 min.

^b VP actinometer; [ACP] = 0.00199 M.

TABLE 38. Quenching of the type II product formation from p-(5-hexen-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 4370$, $\Phi_{II} = 0.16^b$ HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁵ M	Φ_o/Φ
0.0	2.291	28.6	1.00
1.66	1.450	18.1	1.58
4.16	0.841	10.5	2.72
8.31	0.497	6.21	4.61
16.6	0.280	3.50	8.17
24.9	0.182	2.27	12.6

^a [KETONE] = 0.013 M, [MeBz] = 0.00303 M, 313 nm, 30 min.

^b VP actinometer; [ACP] = 0.00578 M.

TABLE 39. Quenching of the type II product formation from p-(9-undecen-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$$k_q \tau = 4400$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[diene], 10 ⁻⁴ M	(Pr/St) _{area}	[type II], 10 ⁻⁴ M	Φ_o/Φ
0.0	2.110	3.06	1.00
0.53	1.696	2.46	1.24
1.32	1.317	1.91	1.60
2.65	0.738	1.41	2.17
5.30	0.627	0.91	3.35
7.95	0.434	0.63	4.88

^a [KETONE] = 0.013 M, [MeBz] = 0.00352 M, 313 nm, 30 min.

TABLE 40. Quenching of the type II product formation from p-(3-methyl-3-buten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 82$, $\Phi_{II} = 0.0037^b$ HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻² M	(Pr/St) _{area}	[type II], 10 ⁻⁵ M	Φ_o/Φ
0.0	0.214	3.93	1.00
0.43	0.164	3.00	1.31
0.85	0.110	2.01	1.96
1.71	0.095	1.74	2.26
2.56	0.0676	1.24	3.17
3.41	0.0556	1.02	3.85

^a [KETONE] = 0.014 M, [MeBz] = 0.00455 M, 313 nm, 2 hr.

^b VP actinometer; [ACP] = 0.00350 M.

TABLE 41. Quenching of the cycloaddition product formation
from p-(3-methyl-3-buten-1-oxy)valerophenone with
2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 94$, $\Phi_{II} = 0.027^b$ GC analysis: 7' QF-1 column
193°C

[diene], 10 ⁻² M	(Pr/St) _{area}	[type II], 10 ⁻⁴ M	Φ_o/Φ
0.0	0.745	9.00	1.00
0.53	0.577	6.97	1.29
1.05	0.434	5.24	1.72
1.58	0.336	4.06	2.22
2.11	0.253	3.06	2.94
3.16	0.194	2.34	3.85

^a [KETONE] = 0.021 M, [C8Bz] = 0.00137 M, 313 nm.

^b VP actinometer; [ACP]_{total} = 0.0112 M.

TABLE 42. Quenching of the type II product formation from p-(3-methyl-3-buten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$k_q \tau = 74$, $\Phi_{II} = 0.0045$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻² M	A _{II} /A _{st}	Φ_o/Φ
0.0	.291	1.00
0.34	.254	1.24
0.68	.201	1.56
1.37	.146	2.16
2.05	.121	2.60
2.74	.105	2.99

a. [KETONE] = 0.012 M, [MeBz] = 0.00477 M.

b. VP actinometer; [ACP] = 0.00413 M.

TABLE 43. Quenching of the type II and the cycloaddition product formation from p-(3-methyl-3-buten-1-oxy) valerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

[diene], 10 ⁻² M	[addn] ^b	Φ_A/Φ_A	A_{II}/A_{st}^c	Φ_o/Φ
0.0	8.85	1.00	3.63	1.00
0.52	6.60	1.34	2.73	1.33
1.03	4.57	1.94	2.01	1.80
1.55	3.63	2.44	1.78	2.04
2.07	3.76	2.35 ^d	1.57	2.31
3.10	2.28	3.88	1.28	2.84

^a [KETONE] = 0.011 M, [CSBz] = 0.00114 M, VP actinometer; [ACP]_{total} = 0.0131 M. ^b Addition product, 10⁻⁴M; GC analysis (7' QF-1 column, 193°C), $k_q\tau = 95$, $\Phi_{II} = 0.022$. ^c Type II product; HPLC analysis (Hexane : EtOAc (98.5 : 1.5), 1.2 ml/min, 270 nm), $k_q\tau = 60$, $\Phi_{II} = 0.0039$. ^d excluded from the calculation.

TABLE 44. Quenching of the photoisomerization of p-(cis-3-hexen-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 58$, $\Phi_{\text{isom}} = 0.27$ ^b HPLC analysis: Ultrasphere Si
Hexane (100)
1.2 ml/min, 270 nm

[diene], 10 ⁻² M	A _{trans} /A _{total} ^c	Φ_o/Φ
0.0	14.7	1.00
0.60	11.0	1.34
1.19	9.1	1.61
2.38	6.4	2.31
3.57	4.5	3.28
4.76	4.1	3.63

^a [KETONE] = 0.011 M, [MeBz] = 0.00464 M, 313 nm, 25 min.

^b VP actinometer; [ACP] = 0.00200 M. ^c area ratio of the trans to the total ketone.

TABLE 45. Quenching of the type II product formation from p-(5-methyl-4-hexen-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 1100$, $\Phi_{II} = 0.040$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[diene], 10 ⁻³ M	(Pr/St) _{area}	[type II], 10 ⁻⁵ M	Φ_o/Φ
0.0	0.780	14.63	1.00
0.34	0.570	10.68	1.37
0.85	0.436	8.17	1.79
1.71	0.258	4.84	3.02
3.41	0.166	3.11	4.70
5.12	0.127	2.39	6.12

^a

[KETONE] = 0.014 M, [MeBz] = 0.00455 M, 313 nm, 30 min.

^b VP actinometer; [ACP] = 0.00350 M.

TABLE 46. Quenching of the type II product formation from p-methoxyvalerophenone with 2-methyl-1-pentene in acetonitrile at 25°C.^a

$$k_q \tau = 2.15$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (98.5 : 1.5)

1.2 ml/min, 270 nm

[quencher], M	(Pr/St) _{area}	Φ_o/Φ
0.0	1.61	1.00
0.098	1.57	1.03
0.246	1.26	1.28
0.492	0.90	1.80
0.983	0.552	2.92
1.475	0.395	4.08

a. [KETONE] = 0.055 M, [C4Bz] = 0.00342 M.

TABLE 47. Quenching of the type II product formation from p-methoxyvalerophenone with 2-methyl-2-pentene in acetonitrile at 25°C.^a

$$k_q \tau = 5.36$$

HPLC analysis: Ultrasphere Si
Hexane : EtOAc (98.5 : 1.5)
1.2 ml/min, 270 nm

[quencher], M	(Pr/St) _{area}	Φ_o/Φ
0.0	3.57	1.00
0.035	2.82	1.27
0.088	2.24	1.59
0.177	2.00	1.79
0.354	1.23	2.90
0.530	0.91	3.91

a. [KETONE] = 0.044 M, [C8Bz] = 0.00187 M.

TABLE 48. Quenching of the type II product formation from γ -vinylvalerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$k_q \tau = 10.2$, $\Phi_{II} = 0.28$ ^b GC analysis: 7' QF-1 column
160 °C

[diene], M	(Pr/St) _{area}	[ACP], 10 ⁻³ M	Φ_o/Φ
.000	0.660	2.18	1.00
.046	0.460	1.52	1.43
.092	0.336	1.11	1.96
.138	0.257	0.85	2.56
.184	0.236	0.78	2.79
.276	0.173	0.57	3.82

^a [KETONE] = 0.030 M, [C17] = 0.00111 M, 313 nm, 1hr.

^b VP actinometer; [ACP] = 0.00257 M.

TABLE 49. Quenching of the type II product formation from γ -vinylvalerophenone with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$$k_q \tau = 14.9, \quad \Phi_{II} = 0.17^b$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (99.2 : 0.8)

1.2 ml/min, 270 nm

[diene], M	(Pr/St) _{area}	[ACP], 10 ⁻⁴ M	Φ_o/Φ
.000	0.565	17.8	1.00
.017	0.464	14.6	1.22
.043	0.365	11.5	1.55
.086	0.263	8.28	2.15
.172	0.162	5.10	3.49
.259	0.117	3.68	4.84

^a [KETONE] = 0.023 M, [C8Bz] = 0.00164 M, 313 nm, 1hr.

^b VP actinometer; [ACP] = 0.00342 M.

TABLE 50. Quenching of the type II product formation from 1-phenyl-5-octen-1-one with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$k_q \tau = 7.1$, $\Phi_{II} = 0.16^b$ GC analysis: 7' QF-1 column
160 °C

[diene], M	(Pr/St) _{area}	[ACP], 10 ⁻⁴ M	Φ_o/Φ
.000	0.281	14.00	1.00
.091	0.164	8.17	1.71
.182	0.133	6.60	2.12
.273	0.105	5.24	2.67
.364	0.0689	3.82	3.66
.546	0.0575	2.86	4.90

^a [KETONE] = 0.030 M, [C16] = 0.00262 M, 313 nm, 3 hr.

^b VP actinometer; [ACP] = 0.00257 M.

TABLE 51. Quenching of the type II product formation from 1-phenyl-6-methyl-5-hepten-1-one with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$k_q \tau = 3.2$, $\Phi_{II} = 0.13$ ^b HPLC analysis: Ultrasphere Si
Hexane : EtOAc (99.2 : 0.8)
1.2 ml/min, 270 nm

[diene], M	(Pr/St) _{area}	[ACP], 10 ⁻⁴ M	Φ_o/Φ
.000	0.1621	8.07	1.00
.077	0.1587	7.90	1.36
.154	0.1193	5.94	1.52
.231	0.0902	4.49	1.80
.307	0.0808	4.02	2.01
.461	0.0571	2.84	2.84

^a [KETONE] = 0.026 M, [C8Bz] = 0.00262 M, 313 nm, 3hr.

^b VP actinometer; [ACP] = 0.00209 M.

TABLE 52. Quenching of the type II product formation from 1-phenyl-6-methyl-5-hepten-1-one with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$k_q \tau = 5.1$, $\Phi_{II} = 0.26^b$ HPLC analysis: Ultrasphere Si
Hexane : EtOAc (99.2 : 0.8)
1.2 ml/min, 270 nm

[diene], M	(Pr/St) _{area}	[ACP], 10 ⁻⁴ M	Φ_o/Φ
.000	0.560	17.3	1.00
.076	0.395	12.2	1.42
.189	0.276	8.52	2.03
.378	0.185	5.73	3.02
.756	0.115	3.57	4.85
1.134	0.067	2.07	8.36

^a [KETONE] = 0.0195 M, [C8Bz] = 0.00161 M, 313 nm, 3hr.

^b VP actinometer; [ACP] = 0.00112 M.

TABLE 53. Quenching of the type II product formation from 1-phenyl-6-cis-nonen-1-one with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$$k_q \tau = 33.5, \quad \Phi_{II} = 0.23^b$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (99.2 : 0.8)

1.2 ml/min, 270 nm

[diene], 10 ⁻² M	(Pr/St) _{area}	[ACP], 10 ⁻⁴ M	Φ_o/Φ
0.00	0.884	14.20	1.00
1.04	0.666	10.70	1.33
2.08	0.532	8.54	1.66
3.11	0.443	7.12	1.99
4.15	0.367	5.89	2.41

^a [KETONE] = 0.022 M, [C8Bz] = 0.00135 M, 313 nm, 45 min.

^b VP actinometer; [ACP] = 0.00229 M.

TABLE 54. Quenching of the type II product formation from 1-phenyl-6-cis-nonen-1-one with 2,5-dimethyl-2,4-hexadiene in acetonitrile at 25°C.^a

$$k_q \tau = 53$$

$$\Phi_{II} = 0.46^b$$

HPLC analysis: Ultrasphere Si

Hexane : EtOAc (99.2 : 0.8)

1.2 ml/min, 270 nm

[diene]	(Pr/St) _{area}	[ACP], 10 ⁻³ M	Φ_o/Φ
0.000	0.366	1.84	1.00
0.068	0.086	0.431	4.27
0.137	0.044	0.222	8.29
0.205	0.031	0.156	11.80

^a [KETONE] = 0.019 M, [C8Bz] = 0.00262 M, 313 nm, 45 min.

^b VP actinometer; [ACP] = 0.00135 M.

TABLE 55. Effects of pyridine on quantum yield for acetophenone formation from 1-phenyl-5-hexen-1-one in benzene at 25°C.^a

GC analysis: 7' QF-1 column
160 °C

[pyridine], M	(Pr/St) _{area}	[ACP], 10 ⁻³ M	Φ_{II}^c
0.000	0.126	0.82	.28
0.258	0.239	1.55	.54
0.515	0.270	1.75	.61
0.773	0.241	1.56	.54
1.03	0.256	1.66	.58
1.55	0.264	1.71	.59

^a [KETONE] = 0.027 M, [C17] = 0.00218 M, 313 nm, 25 min.

^b VP actinometer; [ACP] = 0.00095 M.

^c corrected from the absorption ratio ($\lambda_{313} = 40$).

TABLE 56. Effects of pyridine on quantum yield for acetophenone formation from 1-phenyl-6-methyl-5-hepten-1-one in benzene at 25°C.^a

GC analysis: 7' QF-1 column
160 °C

[pyridine], M	(Pr/St) _{area}	[ACP], 10 ⁻³ M	Φ_{II}^c
.000	0.168	1.09	.200
.203	0.331	2.15	.394
.406	0.373	2.42	.447
.610	0.413	2.68	.495

^a [KETONE] = 0.026 M, [C17] = 0.00218 M.

^b VP actinometer; [ACP] = 0.00193 M.

^c corrected from the absorption ratio ($\lambda_{313} = 40$).

TABLE 57. Quenching of the type II product formation from m-(3-buten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

$k_q \tau = 320$, $\Phi_{II} = 0.0073$ ^b GC analysis: 25' Megabore
160 °C

[diene], 10 ⁻³ M	(Pr/St) _{area}	[type II], 10 ⁻⁵ M	Φ_o/Φ
0.0	0.104	15.6	1.00
0.51	0.0305	4.57	3.41
1.01	0.0210	3.15	4.95
1.52	0.0177	2.65	5.89

^a [KETONE] = 0.010 M, [C₅Bz] = 0.00125 M, 313 nm, 2.5 hr.

^b VP actinometer; [ACP] = 0.00709 M.

TABLE 58. Quenching of the type II product formation from m-(4-methyl-3-penten-1-oxy)valerophenone with 2,5-dimethyl-2,4-hexadiene in benzene at 25°C.^a

GC analysis: 25' Megabore
180 °C

[diene], M	[II], 10 ⁻⁵ M	Φ_o/Φ	A _{un} /A _{st}	Φ_o/Φ
.0000	9.89	1.00	.1346	1.00
.0041	5.66	1.75	.1000	1.35
.0082	4.50	2.47	.0815	1.65
.0122	3.91	2.53	.0732	1.84
.0163	3.17	3.12	.0659	2.04
.0244			.0553	2.43

^a [KETONE] = 0.0077 M, [C₁₀Bz] = 0.00101 M, VP actinometer;

[ACP] = 0.00709 M, 313 nm, 3 hr. ^b Φ_{II} = 0.0038, $k_q \tau$ = 120.

^c Φ = 0.0056 (estimated from GC peak), $k_q \tau$ = 57.

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